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ALKALI ION ANALYSIS OF THERMAL WATERS IN NEW ZEALAND

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(Received for publication, 8 November 1960)

Summary

The flame spectrophotometric method used for analysis of solutions for the ions Li^+, Na^+, K^+, Rb^+, and Cs^+ has been examined. Results of analyses for these ions in thermal waters in New Zealand are presented, and from chloride/alkali ratios a comparison is made of spring water compositions with the local igneous rock types.

INTRODUCTION

Flame photometry is used extensively in analysing for the alkali ions in waters and rocks. Hegedus (1959) in a review on flame analysis gave a large number of references to flame photometry. Important subsequent papers include Pietzka and Chun (1959), Foster and Hume (1959), and Shellenberger, *et al.* (1960). Other methods of analysis such as chemical (Ishibashi, *et al.* 1959, and Ishibashi and Hara, 1959) and neutron activation analysis (Cabell and Smales, 1957), require separation of the alkali ions.

In flame photometry a large number of ions interfere with the emission of the alkalies and in using the method as an analytical tool the degree of interference must be investigated for each system.

EXPERIMENTAL

The analyses were made with a Beckman D.U.spectrophotometer, using the Beckman oxy-acetylene flame attachment. The spectral energy recording apparatus (Sera) attachment was used, coupled to a Sunvic 10 mv recorder.

Mutual interferences of ions in solution were investigated to concentrations greater than would be found in most thermal waters. Table 1 summarises

the mutual interferences of alkali metal ions, while Table 2 lists other ions tested and the concentrations for which no interference was found.

TABLE 1—Mutual Interference of Alkali Ions

Ion to be Determined	Max. Conc.	Li^+ 10 p.p.m.	Na^+ 5,000 p.p.m.	K^+ 500 p.p.m.	Rb^+ 10 p.p.m.	Cs^+ 10 p.p.m.
Li^+	10 p.p.m.	—	very slight enhancement	very slight enhancement	no effect	no effect
Na^+	5,000 p.p.m.	no effect	—	no effect	no effect	no effect
K^+	250 p.p.m.	no effect	enhancement	—	no effect	no effect
Rb^+	10 p.p.m.	no effect	enhancement	enhancement	—	no effect
Cs^+	10 p.p.m.	no effect	enhancement	enhancement	no effect	—

TABLE 2—Concentration of Other Ions Giving No Inference with Alkali Emission

Ion	SO_4^{2-}	HBO_2	HCO_3^-	SiO_2
Concentration	200 p.p.m.	500 p.p.m.	400 p.p.m.	100 p.p.m.

Ion	F^-	As_2O_3	Ca^{2+}	Mg^{2+}	Fe^{3+}
Concentration	20 p.p.m.	25 p.p.m.	100 p.p.m.	10 p.p.m.	500 p.p.m.

Tables 1 and 2 show that the alkali ion emissions are affected appreciably only by the presence of certain other alkali ions. In more detail, Figs 1 and 2 show that the enhancement is not linear. Figure 1 shows the enhancement of the emissions given by 10 p.p.m. Li, 250 p.p.m. K, 10 p.p.m. Rb, and 10 p.p.m. Cs with increasing amounts of sodium chloride in solution. The sodium ion has a small effect on the lithium emission, a slight enhancement of the potassium emission and a strong enhancement of the rubidium and caesium emissions. Figure 2 shows the enhancement of Li, Na, Rb, and Cs emissions with increasing amounts of potassium chloride. At the relative concentrations used, the potassium has a small effect on the lithium emission, no effect on the sodium emission, but a strong enhancement of the rubidium and caesium emissions.

The concentrations of the alkali ions in thermal waters were measured as follows, making due allowance for interference effects.

LITHIUM ION

As the other cations have only a very slight effect on the lithium emission at 6708 Å, AnalaR lithium chloride solutions were used as standards to calibrate the emission intensity/concentrations curves. The limit of detection was 0·02 p.p.m.

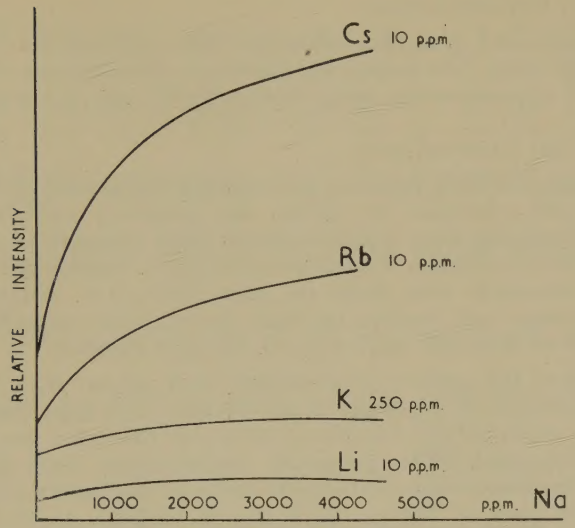

FIG. 1—Effect of increasing Na concentration on Li, K, Rb, and Cs emissions.

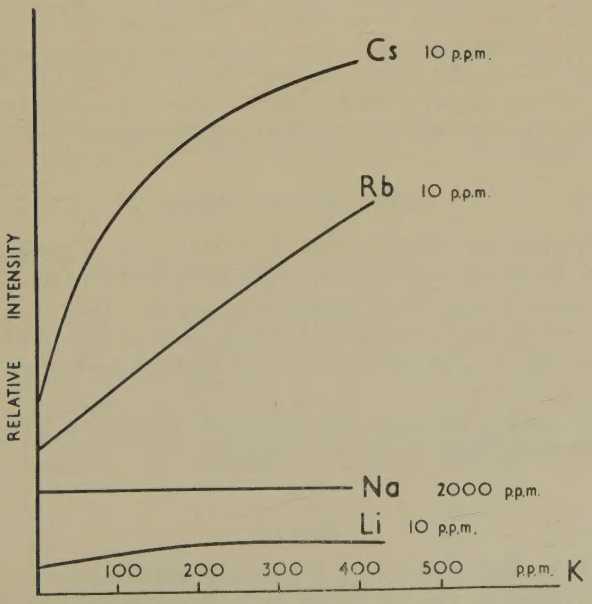

FIG. 2—Effect of increasing K concentration on Li, Na, Rb, and Cs emissions.

SODIUM AND POTASSIUM IONS

The sodium and potassium emissions were measured at 5893 Å, and 7665 Å, respectively. The sodium and potassium concentrations were obtained by successive approximations using varying Na/K ratio calibration curves.

RUBIDIUM AND CAESIUM IONS

As the spectra of both these ions are enhanced considerably by the presence of sodium and potassium, the sodium and potassium concentrations were first determined and then sample solutions were adjusted by additions of NaCl and KCl to contain a total of 2,500 p.p.m. sodium and 250 p.p.m. potassium. Standards were made up with 2,500 p.p.m. sodium and 250 p.p.m. potassium with varying rubidium and caesium concentrations. The normal limit of detection was 0·1 p.p.m. for each element.

It was found that sodium concentrations much greater than 2,500 p.p.m. caused difficulties with blockages in the burner. Since most thermal waters had sodium concentrations less than 2,500 p.p.m, this value was chosen as a satisfactory standard. With potassium concentrations much greater than 250 p.p.m., the band width of the potassium emission became too great, and the rubidium peak at 7800 Å could not be resolved. In most cases the thermal waters had potassium concentrations less than 250 p.p.m. and for the few with slightly greater concentrations a small correction was made.

For most "dilute" waters, when Rb or Cs could not be detected on the original sample, they were concentrated by evaporation in Pt dishes to bring the Na concentration to approximately 2,500 p.p.m.

Using the Sera attachment, the emission spectrum of the adjusted sample was scanned from 6700 Å to 8950 Å to record the lithium line at 6708 Å, the intense potassium line at 7663 Å, two rubidium lines at 7800 Å and 7948 Å, the intense sodium line at 8195 Å, and the two caesium lines at 8521 Å and 8944 Å. Figure 3 shows a typical emission scan. From calibration curves the concentrations of lithium, rubidium and caesium were determined.

HYDROTHERMAL AREAS

Where available the sheet number of N.Z.M.S. 86 is given in Table 3, followed by the spring number allocated by New Zealand Geological Survey.

The Tokaanu springs were described by Healy (1942) and the series numbers given to these springs in Table 3 refer to Fig. 1 in that paper. The terminology for the Banks Peninsula springs is as given by Collins (1953).

Wherever possible the remaining springs are referred to by names which have become established by general usage.

RESULTS

Table 3 shows the results of the analyses for the alkali ions, together with the chloride, sulphate, and pH results for many of the thermal areas in New Zealand.

TABLE 3—Analysis of Thermal Areas in New Zealand

Area	Spring	pH	Cl^- (p.p.m.)	SO_4^{2-} (p.p.m.)	Li^+ (p.p.m.)	Na^+ (p.p.m.)	K^+ (p.p.m.)	Rb^+ (p.p.m.)	Cs^+ (p.p.m.)	Ratio to 3000 p.p.m. Cl^-				
										Li^+ (p.p.m.)	Na^+ (p.p.m.)	K^+ (p.p.m.)	Rb^+ (p.p.m.)	Cs^+ (p.p.m.)
Ruapehu	Crater Lake	..	3925	6420	0·5	305	25	<0·5	0·1	0·4	233	19	..	0·08
,,	,,	..	3977	4330	0·3*	260	50	0·25*	0·05*	0·25	196	38	0·20	0·04
Tongariro	Emerald Lake	3·5	3·55	62	..	10	1	..	..	..	8450	850	..	..
Ketetahi	Upper Red Cascade	6·8	4·26	980	0·05*	50	8	*	*	210	35200	5630	..	..
Tokaanu	Bore 1 (DSIR)	8·7	1775	27	16	1030	95	0·8*	2·3*	27	1740	160	1·4	3·8
,,	Middle pool (Healy, 7)	6·5	3095	79	24	1820	165	1·1	4·7	23	1760	160	1·1	4·6
,,	Bath's source (Healy, 1)	6·9	1239	35	10	740	65	1·0	1·2	23	1790	157	2·4	2·9
,,	Former geyser N side of road (Healy, 14)	7·2	1956	42	14·8	1170	116	1·5	2·6	23	1790	178	2·3	4·0
Waihi	Opposite church	6·7	462	23	4·3*	255	48	0·5*	0·45*	28	1660	310	2·2	2·9
Taupo-Terraces	Pool on flat by baths N94/7/4	8·5	499	94	4·5	410	44	0·2	<0·1	27	2460	260	1·2	..
,,	Head of Flume N94/7/1	8·5	507	109	6·2	420	43	<0·04*	<0·04*	37	2480	250	..	..
Taupo Spa	A.C. Baths N94/7/92	5·7	155	65	0·1	50	7	0·4	0·2	2	1000	140	7·7	4
,,	Paddle Wheel N94/7/56	8·0	1592	43	8·7	1010	70	0·8	1·7	16	1900	130	1·5	3·2
,,	Eunice Geyser N94/7/41	7·8	1427	50	8·0	910	70	1·4	1·0	17	1910	150	2·9	2·1
Waiora	Devil's Eyeglass N94/4/491	3·2	174	258	3·8	410	45	0·5	0·1	66	7070	780	8·6	1·7
,,	Heavenly Twins N94/4/418–419	..	107	..	0·88*	120	16	0·13*	0·04*	25	3380	450	3·7	1·1
Wairakei	Champagne Cauldron N94/4/97	8·0	1770	26	10·8	1070	102	1·1	2·7	18	1810	175	1·9	4·6
,,	"East Spouter" N94/4/231	8·5	1840	260	12·4	1140	85	1·8	1·8	20	1860	140	2·9	2·9
,,	Eagle's Nest Geyser N94/4/131	..	1388	..	9·1	820	48	1·2	2·0	20	1770	104	2·6	4·3
Rotokaua	"Black Geyser" N94/5/65	2·3	671	990	3·6*	505	44	0·5*	1·2*	16	2260	196	2·2	5·3
,,	No. 35 N94/5/35	5·7	2095	288	16·0	1300	92	0·8	2·3	23	1860	132	1·2	3·3
Mokai	Alkaline bath 1 mile S of Geyser Valley	7·0	46	2	0·3	145	10	0·25*	0·1*	6	9520	630	16	6
Mokai-Geyser Valley	Southern end of valley	6·5	6	21	0·04*	90	3	<0·02*	<0·02*	20	45300	1510	..	..
,,	Northern end of valley	..	10	..	0·01*	85	14	<0·02*	<0·02*	10	25500	5200	..	..
Ngatimariki	Large pool	7·3	462	99	4·0	405	27	0·05*	<0·04*	26	2630	175	0·2	..
Ohaki	Large pool	..	1080	56	10·3	1000	57	0·1	1·2	29	2770	160	0·3	3·3
Orakei Korako	Geyser N85/8/16	..	..	..	3·8	350	31	0·24*	0·30*	..	..	..	..	..
,,	"Pudding Basin" N85/8/6	..	302	..	3·3	300	35	0·16*	0·24*	33	2980	350	1·6	2·4
,,	Waipapa Geyser	..	434	62	3·9	345	34	0·3	0·6	27	2320	235	2·1	4·2
Te Kopia	Most southerly of 3 large pools	2·8	16	468	0·14*	35	31	0·32*	0·30*	27	6640	590	59	55
,,	Red Pool	..	22	..	0·17*	45	41	0·40*	0·60*	23	6130	560	55	82
Waikite	Large Pool	7·2	114	32	2·1	180	8	0·8	0·4	55	4730	220	21	8·3
Waiotapu	Champagne Pool N85/6/64	6·5	1880	99	9·2	1150	160	2·2	1·6	15	1830	255	3·5	2·6
,,	Postmistress Pool N85/6/20	8·8	683	71	4·2	470	22	0·3	0·6	19	2070	155	1·3	2·6
,,	Lake Ngahoro Spring N85/6/97	6·6	1785	59	5·9	1120	35	1·0	1·6	10	1880	60	1·7	2·7
Golden Springs	Upper Pool	..	50	..	1·2*	230	22	<0·02*	<0·02*	72	13780	1320	..	..
Waimangu	Echo Lake	..	756	26	3·4	560	48	0·3	0·3	14	2220	190	1·2	1·2
,,	Iodine Spring	9·0	863	99	4·7	610	82	1·1	0·1	16	2120	285	3·8	0·4
,,	Inferno Crater	..	947	185	5·7	550	116	1·4	1·2	14	1320	280	4·4	2·9

TABLE 3—Analysis of Thermal Areas in New Zealand—*continued*

Area	Spring	pH	Cl^- (p.p.m.)	SO_4^{2-} (p.p.m.)	Li^+ (p.p.m.)	Na^+ (p.p.m.)	K^+ (p.p.m.)	Rb^+ (p.p.m.)	Cs^+ (p.p.m.)	Ratio to 3000 p.p.m. Cl^-: Li^+ (p.p.m.)	Na^+ (p.p.m.)	K^+ (p.p.m.)	Rb^+ (p.p.m.)	Cs^+ (p.p.m.)
Whakarewarewa	Pohutu	..	600	11	5·1	412	70	0·4	0·3	26	2060	350	2·0	1·5
,,	Te Horo	8·2	592	119	4·5	470	65	0·6	0·1	23	2380	330	3·0	0·5
,,	Ngararatuatara	8·1	568	65	2·8	400	53	0·7	0·2	15	2110	280	3·7	1·1
Rotorua	Rachel Spring	9·1	558	84	2·3	540	28	0·6	0·2	12	2900	150	3·2	1·1
,,	Golf Link's Bore	..	753	130	1·8	610	27	0·1	0·6	7	2430	107	0·4	2·4
Rotorua-Ohinemutu	Pool opposite Waikite Geyser	8·9	335	41	2·8*	340	17	0·25*	0·5*	25	3045	155	2·0	4·5
Kuirau	High School bore	..	338	90	2·8	345	133	0·3	0·3	25	3060	1180	2·7	2·7
,,	Soda Spring	9·0	216	63	..	320	27	1·1*	1·5*	..	4440	375	15	21
Mokoia Island	Hinemoa's Pool	6·8	67	31	0·74*	150	12	<0·02*	<0·02*	33	6750	540	..	..
,,	North of jetty	..	89	..	0·76*	160	14	<0·02*	<0·02*	25	5390	470	..	..
Lake Rotoiti	Lake shore	9·2	234	82	2·2	270	24	0·02*	<0·02*	28	3450	310	0·3	..
,,	Area in pine plantation	2·4	6·4	1400	0·06	50	10	0·07*	0·04*	28	23450	4690	33	15
Tikitere	Terminal Pool, Korokoro	..	15	..	<0·005*	20	6	<0·02*	<0·02*	..	4100	120	..	..
,,	Ununahua Bath	..	3·6	..	0·03	40	5	<0·02*	<0·02*	25	33300	4170	..	..
,,	Cookson's bore	8·7	320	54	0·9	590	24	<0·04*	<0·04*	8	5540	226	..	..
Ruahine	Large Pool	..	25	..	<0·005*	25	7	<0·02*	<0·02*	..	3020	850	..	..
Waitangi	Soda Pool	..	352	47	1·8	305	24	0·1	0·1	15	2600	205	0·9	0·6
Onepu	Ruruanga, Blue-green Pool	5·6	600	164	3·3	420	48	0·1	0·8	17	2110	240	0·5	4·0
,,	Spring on Tarawera River bank	8·7	355	138	2·6	295	54	0·20*	0·10*	22	2490	460	2·1	1·1
,,	By L. Rotoitipaku – pool to E of lake	7·7	521	91	4·6	360	52	0·26*	0·24*	27	2070	230	1·5	1·3
,,	By L. Rotoitipaku – clear pool to south of lake	..	320	..	1·3	570	27	<0·05*	<0·05*	12	5350	250	..	..
Kawerau	M.O.W. Bore 1	7·5	1095	14	4·6	680	79	0·5	0·5	13	1860	220	1·4	1·4
White Island	Pool in middle of 1933 crater	..	2300	..	5·8	7630	2325	7·7	2·0	8	9960	3040	10·1	2·6
,,	Stream by Seven Dwarfs	..	62600	..	0·05	230	142	0·15	<0·1	0·003	11	7	0·007	..
,,	Large green pool above Noisy Nellie	..	44000	..	4·65	850	139	1·40	<0·1	0·32	58	10	0·10	..
					Warm Springs North Island									
Ngawha	Venus Baths	6·1	186	317	0·9	180	18	<0·02*	<0·02*	15	2900	290	..	..
Ngawha	Milky Way	6·7	228	1260	1·3	210	30	<0·02*	<0·02*	17	2760	295	..	..
Wekaweka		6·4	6120	242	5·7	2520	46	<0·2	0·2	2·8	1240	23	..	0·1
Waiwera	Hotel Baths	..	1110	0·9	1·7	720	8	<0·2	0·2	4·6	1940	22	..	0·5
Tangawahine		7·7	6390	88	10·5	4620	325	<0·2	0·7	4·9	2170	22	..	0·3
Runaruna		8·1	11200	110	25	9200	35	<0·2	0·2	6·7	2470	9	..	0·05
Helensville	Hotel Bore	6·5	1030	1·0	0·8*	600	22	<0·1*	<0·1*	2·5	1780	65	..	..
Warui		..	12	1·1	<0·2	104	15	<0·02*	<0·02*	..	26000	3750	..	..
Te Aroha	CO_2 Geyser	..	518	321	2·0	4670	108	<0·1	<0·1	12	27080	625	..	..
Awakeri	Pukaahu Spring	..	36	29	0·24*	120	8	<0·02*	<0·02*	20	10000	670	..	..
Morere	Baths 1 and 2	..	16000	21	5·4	7100	100	<0·1	<0·1	1·0	1330	19	..	..
Tarawera		..	660	82	1·9	500	9	<0·1	<0·1	8·5	2270	41	..	..
					Warm Springs South Island									
Hanmer	Tank in grounds	..	501	74	1·7	370	40	<0·1	<0·1	9·9	2210	240	..	..
Maruia	Bath supply	..	156	8·3	1·5	155	8	<0·02*	<0·02*	29	2980	150	..	..
Fox Glacier		7·0	185	4	1·3*	335	23	0·03*	<0·02*	21	5430	370	0·5	..
Banks Peninsula	Lyttelton Tunnel	7·1	513	110	..	174	18	<0·02*	<0·02*	..	1020	100	..	..
,,	Cass Bay	7·6	264	1·5	0·3	480	24	<0·04*	<0·04*	3	4220	210	..	..
,,	"Ferrymeade"	7·5	213	24	..	151	6	<0·02*	<0·02*	..	2130	90	..	..
,,	Motukarara Spring	7·9	122	18	..	116	5	<0·02*	<0·02*	..	2850	110	..	..

* Samples analysed after concentration

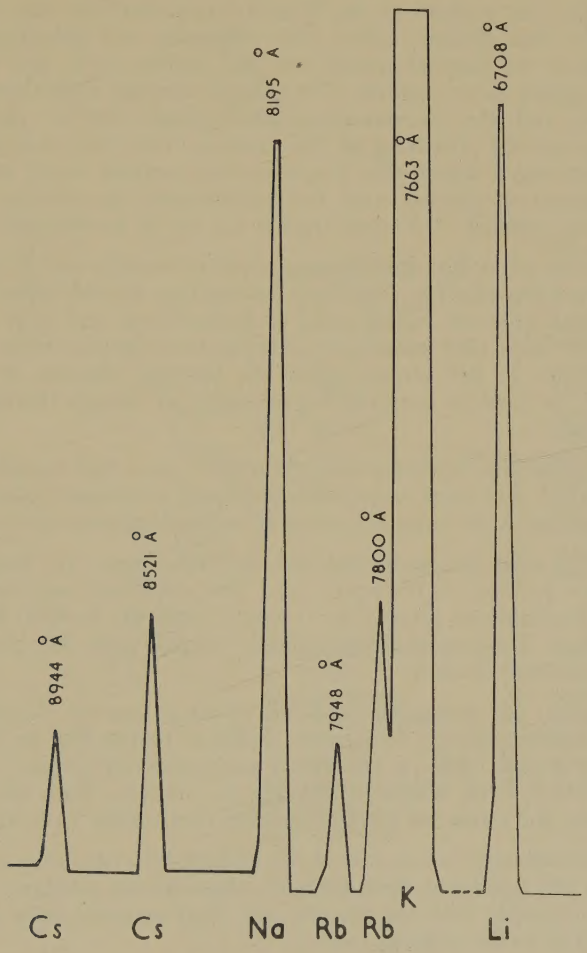

FIG. 3—Alkali metal spectrum.

DISCUSSION

In comparing thermal areas from chemical analysis the problem arises of relating the results on a common basis. Allowance must be made for possible dilution of the thermal water by cold water, leaching from local country rock, and absorption of ions from the water by the rock.

Ions may be carried to the surface thermal waters in liquid or gaseous phases. The ions may be derived from a magmatic source, or may be leached from the country rock during the passage of water to the surface.

From alkali ion analyses in the Wairakei hydrothermal field it has been shown (Ellis and Wilson 1960) that potassium and rubidium ions are absorbed from the thermal waters into the country rock, and to a slight extent this applies also to lithium. The caesium contents were almost constant at Wairakei, and the concentrations were greater than in the unaltered Wairakei ignimbrite. Leaching of the caesium from the country rock was therefore considered improbable. It appears that caesium would make a good basis for comparing thermal areas, but unfortunately the caesium concentration in a large number of thermal areas is too low to be detected.

The chloride ion origin was discussed in detail by Ellis and Wilson, and it appears most likely that the chloride is carried into thermal areas in a liquid phase as alkali chlorides rather than as hydrochloric acid in a gas phase. These authors show that leaching of chloride from igneous rocks appears to be unimportant. In the present paper the chloride contents of the water samples will be used to compare the chemistry of various thermal areas in New Zealand.

Table 3 shows the concentrations of the alkali ions that would be present in the waters if they were evaporated or diluted to contain 3,000 p.p.m. of chloride. This gives the ratios as a series of numbers of convenient magnitude.

The thermal areas can be divided into two broad types: (a) Rubidium and caesium ions present, $> 0{\cdot}1$ p.p.m. and (b) rubidium and caesium ions either not detectable or present just a trace. Type (a) thermal areas all lie in a belt from Tokaanu to White Island, whereas type (b) covers all the other areas in New Zealand.

An important fact emerging from this survey is that for thermal areas in the North Island volcanic areas from Tokaanu to the Bay of Plenty (see Fig. 4), the caesium ratios in the waters are remarkably similar (1–5), with the exception of a few waters usually low in chloride. With the same type of exceptions, the ratios for lithium are also very similar (10–30).

The potassium ratios are usually of the same order (100–300) in the above area, as are the rubidium ratios (0·3–4). However, as rubidium and potassium interact readily with the country rock their concentrations will not be directly related to the original source.

The small differences in the caesium and lithium ratios within this area suggest that the thermal waters arise from similar origins, or even from a common origin. The chemistry of the alkali ions reflects the consistent basic geological pattern in this area of rhyolite, pumice, and ignimbrites.

Further evidence for a similar or common origin of the thermal waters in this area comes from the results on arsenic given by Ritchie (1960). The arsenic versus chloride results for waters show a definite relationship.

Table 4 gives a summary of the alkali results for some of the main New Zealand areas, together with results from Yellowstone National Park (Gooch and Whitfield, 1888), Nevada (White, *et al.*, 1953) and two areas in Iceland (pers. comm. to A. J. Ellis by G. Bodvarsson). It is unfortunate that rubidium and caesium have not been determined in other areas but the lithium values may be compared.

FIG. 4—North Island thermal areas.

High caesium, rubidium and lithium values are found in areas of rhyolite material, while in andesitic and basaltic areas such as Banks Peninsula, Ruapehu, and Iceland these elements are in low concentration ratios.

In acid sulphate pools formed by oxidation of sulphur compounds at or near the surface, cations have been leached from surface rocks. These pools are usually steam-heated, and the alkali constituents have little relationship to the composition of the original hydrothermal fluid. Examples are Tikitere, Te Kopia.

Most rock types contain at least several parts per million of lithium (Horstman, 1957), so it is not surprising that small quantities of this element are found in most pools as a result of simple rock leaching. It is doubtful whether lithium values above about 1 p.p.m. can be derived in this way. Preliminary work in Dominion Laboratory has also shown that the

major surface igneous rock types of the Central North Island contain less than 1 p.p.m. caesium. Spring waters do not usually derive their caesium contents by surface leaching. However, the rubidium and caesium contents are higher at Te Kopia and Kuirau than would be expected from the general water compositions and are difficult to explain other than by a local surface source of these elements.

TABLE 4—Comparison of Li^+, Na^+, K^+, Rb^+, and Cs^+ Ratios to 3,000 p.p.m. Cl^- for a Number of Thermal Regions

Country	Region	Ratios to 3,000 p.p.m. Cl^-				
		Li^+ (p.p.m.)	Na^+ (p.p.m.)	K^+ (p.p.m.)	Rb^+ (p.p.m.)	Cs^+ (p.p.m.)
New Zealand	Ruapehu	0.3	220	30	0.2	0.06
„	Tokaanu-Waihi	24	1750	170	1.5	3.6
„	Taupo, Spa	16	1900	140	2.2	2.6
„	Wairakei (Geyser Valley)	19	1800	120	2.7	3.5
„	Wairakei (bores)	19	1800	310	3.7	3.3
„	Orakei Korako	29	2600	290	1.8	3.2
„	Waiotapu	16	1900	200	2.4	2.6
„	Whakarewarewa	23	2100	320	2.9	1.1
„	Rotorua	10	2600	120	2.5	1.8
„	Rotorua (bores)	25	3100	120	2.7	2.7
„	Onepu-Kawerau	20	2000	230	1.6	1.3
„	Kawerau (bore)	13	1900	220	1.4	1.4
„	Helensville	2.5	1800	65	<0.3	<0.3
„	Ngawha	16	2800	290	<0.3	<0.3
„	Banks Peninsula	3.0	2500	130	<0.5	<0.5
„	Hanmer	9.9	2210	240	<0.5	<0.5
Iceland	Krisuvik (bore B14)	2.5	2040	278	—	—
„	Haukadalur (Spring)	4.8	5550	262	—	—
U.S.A.	Yellowstone Park	31	3500	220	—	—
„	Nevada (No. 21 Steamboat Springs)	16	2300	240	—	—

It may be noted that the potassium ratios for the waters are not very sensitive to the igneous rock environments. The values for Banks Peninsula and Iceland differ little from those for Yellowstone and Wairakei.

Healy (1942) in a discussion of the hot-springs at Tokaanu considered that the heat and chemicals were derived from a cooling andesite intrusion beneath the area. The present results suggest that the spring waters at Tokaanu and Waihi have the same type of origin as those in the other northern thermal areas within the graben. The high level of rubidium and caesium is suggestive more of a magma enriched in alkalis such as a partly crystallised rhyolite intrusion.

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LABORATORY TESTS OF SOME INSECTICIDE AND ANTIBIOTIC TREATMENTS AGAINST LARVAE OF THE AUSTRALIAN CARPET BEETLE (*Anthrenocerus Australis* (HOPE))

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Summary

Effective control of carpet beetle larvae (measured by fabric weight loss and frass weight methods) was obtained with dusts containing 0·8% pyrethrum extract (25% pyrethrins) + 2% piperonyl butoxide combined with 0·5%–5·0% gamma benzene hexachloride or with 2·0% chlordane. All these dusts gave complete knockdown or kill of test larvae within the two weeks duration of the experiment. Treatment of fabric with borax powder, or a hot aqueous solution of boric acid, or with dilute aqueous solutions (33 p.p.m.) of cycloheximide or thiolutin was ineffective.

INTRODUCTION

The Australian carpet beetle (*Anthrenocerus australis* (Hope)) has been an increasingly serious domestic pest since it was first recorded in this country (Lamb, 1950). It attacks carpets and all types of woollen materials and is highly resistant to most of the usual household insecticides. Fabrics can be effectively treated with permanent proofing agents in the manufacturing process but there is still a need for a practicable household treatment of relatively low human toxicity.

Although oil-based sprays of DDT and gamma benzene hexachloride are widely used, they are slow acting and have a relatively low contact toxicity towards carpet beetles (Harrison, 1948). They tend to act as repellents rather than toxicants. We have found that pyrethrum dusts with the synergist piperonyl butoxide (PBO) provide a highly effective knockdown but are of low toxicity towards carpet beetle larvae. Tests were therefore undertaken with pyrethrum-PBO dusts containing BHC or chlordane as the toxic agent. Borax (as a dust) and boric acid (as a wet fabric treatment) were also tested.

Two antiobiotics, cycloheximide and thiolutin were included in these experiments. Cycloheximide (trade name: Actidione) has an antibiotic effect on many yeasts and fungi and has also been used as a rat repellent (Traub *et al.*, 1950). Thiolutin inhibits the growth of many bacteria, fungi, and protozoa (Spector, 1957). These compounds were applied to fabrics in low concentrations (33 p.p.m. aqueous solution) in the hope that they might interfere with the gut microflora of the carpet beetle larvae. Their effect however was negligible.

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MATERIALS AND METHODS

DUSTS:

1. 0·8% pyrethrum extract (25% pyrethrins)
   2·0% piperonyl butoxide
   0·2% hydroquinone (anti-oxidant)
   0·5% gamma benzene hexachloride
2. 0·8% pyrethrum extract (25% pyrethrins)
   2·0% piperonyl butoxide
   2·5% gamma benzene hexachloride
3. 0·8% pyrethrum extract (25% pyrethrins)
   2·0% piperonyl butoxide
   5·0% gamma benzene hexachloride
4. 0·8% pyrethrum extract (25% pyrethrins)
   2·0% piperonyl butoxide
   2·0% chlordane
5. Borax

WET APPLICATIONS:

6. Boric acid
7. Cycloheximide: 33 p.p.m. aqueous solution + Teepol
8. Thiolutin: 33 p.p.m. aqueous solution + Teepol

White, woollen flannel was punched into one inch diameter discs weighing approximately 90 mg each. Dusts were applied as follows: Eight weighed fabric discs were placed in 4 oz screwcap jars with 0·5 g of dust and shaken by hand. The surplus dust was shaken off the discs which were then reweighed and their dust content calculated. Boric acid was applied from a nearly saturated aqueous solution containing one drop of Teepol wetting agent. This was heated to 90°C and the fabric discs were immersed for 30 min as the solution cooled. They were then rinsed in distilled water and dried. The antibiotic solutions were applied from a pipette so that each disc received 12·6 μg of antibiotic.

The average amount of insecticidal material applied in each treatment is given in Table 1. Four discs were used for tests with 10 large *A. australis* larvae on each, and four were used as humidity checks. The test procedure used was that of Lamb (1950), the discs being exposed to the test insects for two weeks.

TABLE 1—Mean Concentrations of Test Materials Applied to Discs (as per cent w/w on air-dry weight of Fabric)

Treatment	*Concentration* (per cent w/w)
1. Pyrethrum + PBO + HQ + 0·5% BHC	24·4
2. Pyrethrum + PBO +2·5% BHC	27·1
3. Pyrethrum + PBO + 5·0% BHC	29·2
4. Pyrethrum + PBO + 2·0% chlordane	30·9
5. Borax powder	14·0
6. Boric acid	0·73
7. Cycloheximide	0·0135
8. Thiolutin	0·0134

RESULTS AND CONCLUSION

All the pyrethrum dust formulations gave complete knockdown or kill of test larvae but the mortality of larvae in the borax, boric acid, and antibiotic treatments did not differ significantly from the untreated checks.

Frass weights and fabric weight loss were calculated by the method of Lamb (1951) and the results subjected to analysis of variance (see Table 2). All the dusts containing pyrethrum gave results significantly better than the checks – whether determined by frass weight or fabric weight loss. The efficiencies of these treatments were between 86 and 102% and they could therefore be considered economically effective. Although the borax treatment resulted in significantly less fabric weight loss than the check, the amount of frass produced was not significantly less than the check. This treatment showed considerable variation between the replicates and this might have been due to the larger particle size of the dust and thus less uniform treatment of the test fabric. The remaining treatments were not significantly different from the checks and must be considered ineffective.

TABLE 2—Mean Frass Weights and Fabric Weight Loss of Treated Discs

Treatment	Frass Wgt. (mg)	Calculated % Efficiency (From Frass Weights)	Fabric Wgt. Loss (mg)	Calculated % Efficiency (From Wgt. Loss)
1. Pyrethrum PBO + 0·5% BHC ..	0·8**	91	2·3**	89
2. „ + 2·5% BHC ..	1·3**	86	1·3**	94
3. „ + 5·0% BHC ..	0·7**	92	0·0**	100
4. „ + 2·0% Chlordane	0·6**	93	−0·5**	102
5. Borax dust	8·0	5	5·6**	74
Dust check (untreated)	8·40	..	21·3	..
6. Boric acid	2·43	29	3·4	46
Boric acid check (untreated) ..	3·33	..	6·2	..
7. Cycloheximide	4·4	28	7·9	29
8. Thiolutin	5·4	10	9·9	11
Antibiotic check (untreated)	6·0	..	11·2	..

(**Significantly different from checks at 1% level)

These results suggest that the incorporation of a knockdown agent with insecticidal dusts enhances their efficiency against carpet beetle larvae. The rapid knockdown effect results in an immediate cessation of feeding and also enforces prolonged exposure to the slower acting insecticidal component. These materials would merit trial under domestic conditions.

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ARSENIC AND ANTIMONY IN SOME NEW ZEALAND THERMAL WATERS

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Summary

The arsenic and antimony contents of thermal waters, mainly of the North Island, have been determined. Arsenic results span a period of eight years. The results are discussed from a geochemical standpoint: arsenic, with chloride, suggests a family relationship between the Rotorua-Taupo region waters; the significance of antimony is lost through deposition and reworking; comparison is made with waters outside New Zealand.

INTRODUCTION

Arsenic has been known to occur in thermal waters in New Zealand since Grimmett and McIntosh (1939) reported its presence in waters and sinters at Waiotapu. In 1954–55, in a survey of hydrothermal activity, a large number of samples of thermal waters, from natural hot springs and from drillholes, was analysed for arsenic. This work was done by A. J. Ellis, the samples having been collected by S. H. Wilson and A. J. Ellis; the results have not previously been published. More recently, antimony was found in Wairakei bore water and it became of interest to survey the occurrence of the pair, arsenic and antimony, in the Rotorua-Taupo thermal region; sampling and analysis were done by the present author.

The power project has been described by Smith (1958). The natural activity in the Rotorua-Taupo region was described by Grange (1937), who gave analyses of many waters. New analyses of those springs now resampled show, in general, very little change. But Ohaki pool, described in 1937 as clear and bordered with white sinter, since mid-1957 (Miss M. White, pers. comm.) carries a red-orange flocculent precipitate which is being deposited over the white sinter. Spectrographic analysis showed the presence of about 10% of antimony in this precipitate.

EXPERIMENTAL

Samples

Natural springs were sampled at a point of maximum flow as close as possible to the source, usually near the outlet of the pool, and geysers during a discharge. Bore discharges were sampled at atmospheric pressure, through a separator (Ellis and Wilson, 1960), or from the edge of the blast issuing

from horizontal silencers or from the weir box of twin-tower silencers. At Bore 211, Wairakei, only a trickle of water from the flange at the end of the bypass could be collected – not a good sample.

In the earlier work the samples were filtered through asbestos mats into glass bottles. In 1959, 5l pyrex bottles were filled with the water; most samples remained crystal clear but a slight sediment settled in some; these latter were shaken up before taking the portion for analysis. The waters of Champagne Pool, Waiotapu, and Ohaki Pool had flocculent precipitates and the Champagne Pool water became cloudy-yellow on cooling. These samples were filtered through sintered glass and the precipitates were assayed separately; the Champagne Pool filtrate was cloudy and was used without further ado.

The Waikato River water was sampled at Taupo, just below the control gates, at the Aratiatia rapids, and at the Whakaheke rapids: places of turbulent flow were chosen to ensure homogeneity of the stream at the sampling point. The portions for extraction were decanted from such sediment as settled out.

Calcite and silica which had been deposited on the casing in bores at Wairakei were recovered by Ministry of Works in the course of cleaning operations; clean colourless material was selected for the present work. Specimens of siliceous sinter were collected from the flumes carrying the discharged water to waste.

Separation and Determination of Arsenic and Antimony

The earlier determinations of arsenic were done by the standard method published by the American Public Health Association (1946, pp. 46–47), in which arsenic is separated as arsine, absorbed in sodium hypobromite solution and determined photometrically as molybdenum blue.

The procedures used in the later work were mainly adapted from those of Wyatt (1955). A 3l sample of water was made normal in sulphuric acid and treated with thioglycollic acid, potassium iodide, and ascorbic acid. It was then extracted with a chloroform solution of diethylammonium diethyldithiocarbamate; excess of reagents was used to ensure complete recovery. Previous work had shown that no interference by copper and bismuth could be expected. After removal of the chloroform by distillation, the residue was digested with sulphuric acid and ammonium sulphate, the solution was made to 50 ml in a standard flask and aliquots were taken for the determinations. The sum of arsenic and antimony was determined, on a 25 ml aliquot, by titration with standard potassium bromate, using α-naphthoflavone indicator. Arsenic was found by difference after determination of antimony by one of two methods: (i) a Rhodamine B and benzene extraction procedure, adapted from Webster and Fairhall (1945), was applied to a 5 ml aliquot (the isopropyl ether extraction method could not be used for lack of that solvent); (ii) if more than 200 μg of antimony was found, the iodoantimonite method, Wyatt (1955), was applied to a 10 ml aliquot. When less than 1 mg of arsenic plus antimony was found by titration, arsenic was determined as molybdenum blue on a 5 ml aliquot.

To test the procedure, standard amounts of arsenic and antimony, comparable with those found in the samples, were added to 3l portions of distilled water and put through the whole operation; four such standards and a blank were run.

The river water samples (5l) were extracted and worked up by the same procedures, with suitable modification, and the whole extract was used for a determination of arsenic by the molybdenum blue method; a standard was also run.

Samples of silica and precipitates were fused with sodium hydroxide, then dissolved with hydrochloric acid; calcite was simply dissolved with hydrochloric acid. Extraction and determination were carried out as before, with suitable scaling down of volumes.

Determination of Chloride

Chloride was determined, in the earlier work, by potentiometric titration with silver nitrate (Kolthoff and Kuroda, 1951), and in the later work by the Mohr method. River waters were first concentrated by evaporation.

RESULTS

Table 1 lists the waters sampled, the date (month and year) of sampling, the analytical results and the calculated atomic ratios chloride/arsenic and arsenic/antimony. The two waterborne precipitates are also included. As far as possible the springs are identified by the numbers given them by the New Zealand Geological Survey. Tokaanu springs were numbered by Healy (1942). Two analyses are taken from unpublished Dominion Laboratory reports.

The A.P.H.A. method for arsenic is known to give good results in experienced hands. The accuracy of the later arsenic and antimony determinations is to be judged from the recoveries got with the standards and shown in Table 2; they tend to be about 5% low and the antimony recovery may be somewhat erratic. The blanks, 0·08 mg As equivalent in the titration and 3 μg Sb by Rhodamine, were satisfactorily low, but when little arsenic or antimony was present in a sample (e.g., Rotorua, Orakei-Korako) the blanks became a significant proportion (7% to 35%) of the total recovered. Internal evidence in Table 1 shows that the two sets of arsenic results are comparable.

Table 3 shows the arsenic and chloride contents of the water of the Waikato River above and below the thermal areas it drains. The standard which was run to check the procedure at this low level of arsenic content had 5 μg of As_2O_3 in 3l; 6 μg were recovered. Blanks were about 0·5 μg/l.

TABLE 1—Arsenic and Antimony in Thermal Waters

Area	Source	Date	Cl^- p.p.m.	As p.p.m.	Sb $\mu g/l$	Atomic Ratios Cl/As	Atomic Ratios As/Sb
Ruapehu	Crater Lake	1/55	3,950	0·14		59,000	
Tokaanu	D.S.I.R. Bore 3	/52	2,020	5·4		790	
	Domain Bath's Source. No. 1 (Healy, 1942)	6/55	1,240	3·4		770	
	D.S.I.R. Bore 1	1/59	1,760	3·9	340	950	19
	Taumatapuhipuhi Geyser. No. 13 (Healy, 1942)	1/59	2,850	6·3	680	950	15
Taupo, Terraces	Head of Flume N 94/7/1	1/54	490	0·4		2,700	
Spa	Paddle Wheel Geyser /56	1/54	1,590	3·2		1,000	
	Eunice Geyser /41	1/54	1,400	2·8		1,100	
	A.C. Baths /92	6/55	16	<0·02		> 2,300	
Huka Falls	Huka Spring N 94/4/628	5/51	710	1·5		980	
	Bore 11	7/53	1,240	2·4		1,100	
Rotokaua	Lake front N 94/5/10	5/51	540	0·24		950	
	Black Geyser /65	5/51	670	1·5		3,000	
Wairakei	Bore 2a	7/53	500	1·0		1,100	
	4/1	6/55	2,090	4·3		1,000	
		1/59	2,100	4·0	85	1,100	76
	4/2	6/55	2,080	4·2		1,000	
	11	1/59	2,190	4·1	120	1,100	56
	12	12/52	1,820	4·2		920	
	13	12/52	1,970	4·6		910	
	18	9/55	2,120	4·2		1,100	
		1/59	2,190	3·9	90	1,200	71
	19	1/59	2,290	3·9	90	1,200	70
	20	1/54	2,260	5·2		920	
	21	10/53	1,750	3·6		1,000	
	24	9/55	2,170	4·4		1,000	
	26	7/55	2,200	4·2		1,100	
	30	1/59	2,240	4·0	105	1,200	62
	37	1/59	2,180	3·8	100	1,200	62
	43	1/59	2,140	4·2	105	1,100	66
	211	1/59	2,390	4·4	90	1,100	79

TABLE 1—Arsenic and Antimony in Thermal Waters—*continued*

Area	Source		Date	Cl^- p.p.m.	As p.p.m.	Sb μg/l	Atomic Ratios Cl/As	As/Sb
Waiora Valley	Devil's Eyeglass	N 94/4/491	5/51	660	1·0		1,400	
	Blue Pools	/418–419	5/51	110	0·23		1,100	
Geyser Valley	Eagle's Nest Geyser	/131	11/54	1,390	3·2		930	
	Haematite Geyser	/85	11/54	1,420	3·0		1,000	
	Devil's Inkpot	/217	11/54	1,270	2·6		1,000	
	Champagne Cauldron	/97	1/59	1,550	2·4	115	1,300	34
	Dancing Rock Geyser	/190	1/59	1,720	3·0	140	1,200	34
Ohaki	Large Pool		5/51	1,040	1·6		1,400	
			7/55	1,080	1·6		1,500	
			1/59	1,110	1·0	900	2,400	2
	precipitate		1/59	..	0·00	44	..	0
Orakei-Korako	Orakei Geyser	N 85/8/16	6/55	390	0·68		1,200	
	Waipapa Geyser	/24	6/55	430	0·66		1,400	
			1/59	400	0·10	30	8,400	5
	Devil's Throat Geyser	/43	1/59	300	0·26	17	2,400	25
	Hochstetter Pool	/98	1/59	300	0·32	20	2,000	26
	Spring, W. Bank, Upstream	/516	1/59	360	0·25	48	3,000	8
Waiotapu	Postmistress Pool	N 85/6/20	6/55	680	1·1		1,300	
			1/59	690	0·2	115	6,600	3
	Champagne Pool	/64	6/55	1,880	5·5		720	
			1/59	2,000	4·9	34	860	240
	precipitate		1/59	..	0·15	420	..	0·6
	Spring by Lake Ngakoro	/97	6/55	1,790	7·9		480	
	Bore 6		1/59	1,450	1·0	215	3,100	7
Waikite	Large pool		6/55	110	0·26		920	
Waimangu	Iodine Spring		6/55	870	1·0		1,800	
	Echo Lake, S.W.		6/55	760	0·59		2,700	
	N.E.		6/55	760	0·52		3,000	
	Echo Lake		1/59	770	0·5	38	3,400	21
Whakarewarewa	Spring, N. shore, Roto-a-Tamaheke		7/55	570	0·29		4,100	
	Ngararatuatara		7/55	540	0·52		2,200	
	Te Horo		7/55	590	0·37		3,400	
	Pohutu Geyser		1/59	570	0·06	36	20,000	3

Rotorua	Golf Links Bore	7/55	730	0·34		4,500	
	Rotorua Post Bore	7/55	410	<0·03		>4 × 10⁴	
	Battersby Motors Bore	7/55	460	<0·02		>4 × 10⁴	
	High School Bore	7/55	340	0·08		9,000	
	Soda Spring, Kuirau Park	7/55	310	0·15		4,300	
	Rachel Spring	7/55	560	0·04		31,000	
		1/59	540	0·01	8	>10⁵	1
Ohinemutu	Pool opposite Waikite Geyser	7/55	340	0·09		7,800	
Te Puia	Baths	4/55	8,200	<0·01		>2 × 10⁶	
Kawerau	M.O.W. Bore 1	7/54	1,110	2·4		950	
Waitangi	Soda Pool	7/55	350	0·03		25,000	
	Waitangi Spring	7/55	330	0·05		13,000	
White Island	Pool 100 yds. S.E. of Seven Dwarfs	11/49	56,300	0·88		134,000	
	Stream draining Seven Dwarfs	11/49	62,700	7·2		18,500	
	Pool in 1933 Crater	11/49	81,600	8·5		20,100	
Te Aroha	Domain, new bore (Dom. Lab. No. C179)	11/36	580	0·4		3,100	
Helensville	Domain baths	5/54	950	0·06		32,000	
	Hotel bore	5/54	1,030	0·02		160,000	
Waiwera	Domain	5/54	1,120	<0·02		>18 × 10⁴	
	Hotel Baths	5/54	1,110	<0·02		>17 × 10⁴	
Ngawha	Jubilee Bath (Dom. Lab. No. K922/1)	3/44	930	0·2		9,800	
Banks Peninsula	Ferrymeade	1/55	290	<0·01		>8 × 10⁴	
	Lyttelton Tunnel	1/55	510	<0·01		>14 × 10⁴	
	Cass Bay	1/55	260	<0·01		>7 × 10⁴	
	Motukarara Spring	1/55	120	<0·01		>3 × 10⁴	

TABLE 2—Recovery of Added Arsenic and Antimony

Arsenic, as As_2O_3			Antimony, as Sb		
Added p.p.m.	Recovered p.p.m.	%	Added µg/1	Recovered µg/1	%
5	4.78	96	100	98	98
0.33	0.32	95	23	23	100
1.67	1.54	93	67	57	85
8.33	7.95	96	670	635	95

TABLE 3—Arsenic and Chloride Content of Waikato River Water

Locality	As_2O_3 µg/1	Cl^- p.p.m.
Taupo	0.5	9
Aratiatia rapids	7	25
Whakaheke rapids	<2	27

DISCUSSION

The relationship between arsenic and chloride in the waters is shown in Fig. 1, in which the arsenic results in Table 1 have been plotted against those for chloride. Points for Ruapehu, Te Puia, and White Island waters are not included as they would lie away to the high chloride side. The plot strongly suggests a family relationship between the thermal waters of the Rotorua-Taupo region. They may be regarded as constituting a main sequence, with only a few exceptions that have relatively less or more arsenic than the generality. For example, the points for Bore 6, Waiotapu, and the spring by Lake Ngakoro fall to the low and high arsenic side respectively of the main trend in Fig. 1. The waters of the Rotorua-Taupo region occur in the central rhyolite plateau; those outside this region all occur in andesite, basalt or sedimentary country and are characterised by uniformly low arsenic contents relative to chloride.

Onishi and Sandell (1955) dealt with the geochemistry of arsenic. They sought a relationship between arsenic and chloride in thermal waters and found that, in those of the Norris Basin, Yellowstone Park, arsenic tended to zero at about 150 p.p.m. chloride and rose exponentially with chloride. In Fig. 1 no indication of an exponential rise of arsenic with chloride appears, but arsenic does tend to zero with chloride at about 450 ± 250 p.p.m.

The small variation in the chloride/arsenic ratio among the Wairakei bore waters is consistent with the generally uniform composition of the waters over the field (Ellis and Wilson, 1960) and no significant change has occurred in the seven years covered. Appreciable increases in the chloride/arsenic ratio have occurred at Waiotapu, Orakei-Korako, Ohaki, Geyser Valley, and Tokaanu. No factor common to these areas is known which could account for the changes. Drilling could be invoked at Waiotapu, but there has been

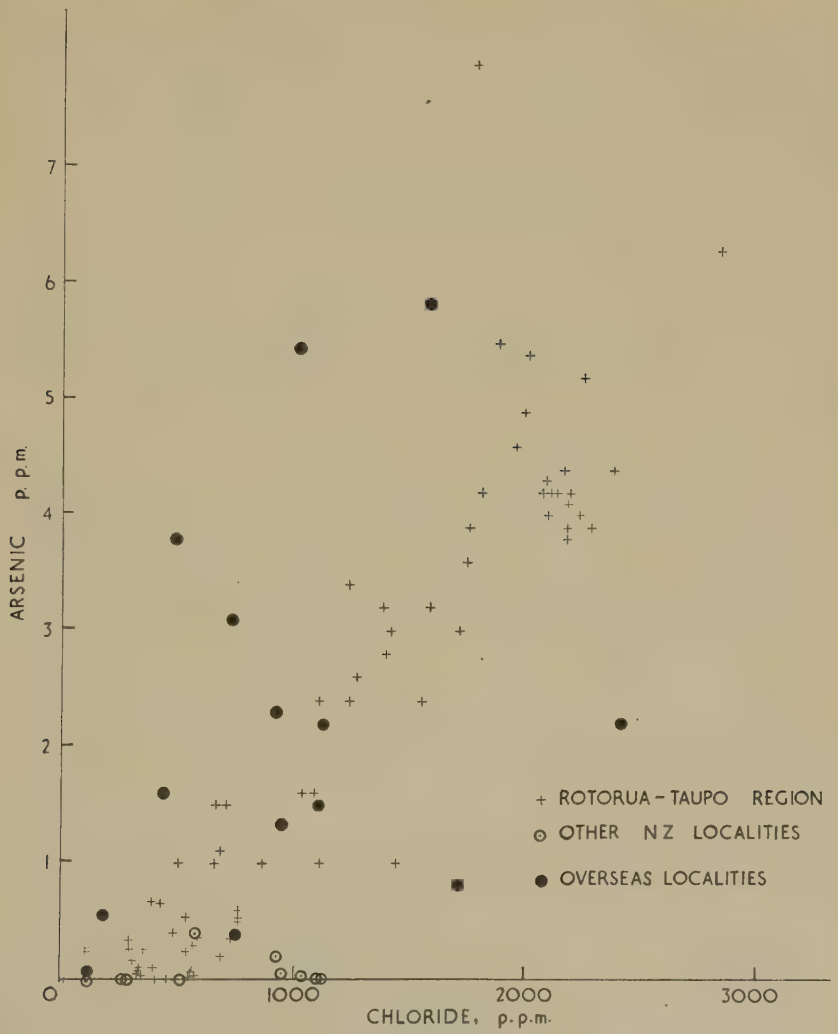

FIG. 1—Relation between arsenic and chloride contents of thermal waters.

very little draw-off by the bores there. On the other hand, the greatly increased draw-off of water at Wairakei may account for the change at Geyser Valley. Thompson (1960) has shown that the chloride content of the waters at Geyser Valley has decreased and questions whether the drilling programme at Wairakei could be responsible.

There is evidence, both chemical (Ellis and Wilson, 1960) and hydrological (Studt, 1958), that the natural activity at Geyser Valley is fed from the aquifer that is tapped by the Wairakei bores, the water flowing in the general direction from the bores to Geyser Valley. A comparison of the results for the bore and Geyser Valley waters shows that the chloride/arsenic

ratios are consistent with the evidence, a little arsenic being lost to the country on the way to the valley. With increased draw-off at Wairakei and decreased flow to Geyser Valley the travel would be slower and arsenic deposition on the way relatively greater.

The chloride-arsenic ratio at Waiora suggested that Waiora was part of the Wairakei field, as was subsequently confirmed by drilling. The values of the ratio at Huka and Taupo Spa suggest that "Wairakei type" water extends southwards at least as far as the Spa.

The fate of the arsenic brought to the surface in the bore water at Wairakei is shown by the results in Table 3: the arsenic, which is discharged into the Waikato River, very rapidly disappears from the water. That it is probably precipitated on the mud is borne out by a test on muddy Waiotapu Stream water. A sample was filtered and the mud and water were assayed separately: 70 μg and 4 μg of arsenic per litre of water was found in the mud and water respectively.

The geochemistry of antimony is not so well known. The variation in the arsenic/antimony ratio among the Wairakei bore waters is twice that to be expected from the experimental error shown in Table 2, but there are not enough results for it to be correlated with anything else at present known about the bores; the very different ratio in the silica deposited in Bore 24 suggests that the variation may be related to silica deposition in the country. Comparison of the ratios for the bore and Geyser Valley waters shows the antimony concentration in the valley doubled relative to arsenic and chloride; assuming the relationship between these waters suggested above, this must mean that the water is reworking earlier hydrothermal deposits enriched in antimony. It may be noticed that the situation of, and the low arsenic antimony ratio at, Bore 11 could mean that this bore taps water on the way to Geyser Valley.

It is conceivable, in a general way, that, if antimony-enriched deposits formed in the past are reworked by water at high temperature, water enriched in antimony could result. The recent change at Ohaki is significant. Considerable deposition of white siliceous sinter has taken place in the past (Grange, 1937), but now an antimony-rich siliceous precipitate is being brought to the surface. Conditions at Steamboat Springs, Nevada, as described by Brannock *et al.* (1948), may be compared: these authors gave analyses showing antimony enrichment in siliceous muds; they supposed that precipitation takes place chiefly a few tens of feet below the surface and the precipitate is carried up mechanically. This appears to be the case at Ohaki where, it is now suggested, a solution step at a deeper level has

TABLE 4—Arsenic and Antimony in Deposits

	As p.p.m.	Sb p.p.m.	As/Sb Atomic
Silica, bore 24, 1192 ft, Wairakei	45	135	0.5
Silica, bore 53, surface, Wairakei	8	185	0.05
Calcite, bore 27, Wairakei	0	0	–
Calcite, bore 44, Wairakei	0	0	–

TABLE 5—Arsenic and Antimony in Thermal Waters Outside New Zealand

Locality	Reference	Cl^- p.p.m.	As p.p.m.	Sb p.p.m.	Atomic Ratios Cl/As	As/Sb
Nevada, Steamboat Springs, hot well	1	747	0·38	0·14	4,200	4
spring 27	1	949	1·35	0·36	1,500	6
Siliceous mud, spring 27	1		0·035%*	3·95%*		<0·02
spring 21	2	921	2·3	0·2	900	18
California, Morgan Springs, Black Growler	3	2,427	2·2	0·0	2,300	..
Wyoming, Yellowstone Park, Shoshone Basin	4	194	0·53	..	770	..
Upper Basin	4	439	1·6	..	580	..
Norris Basin	3	744	3·1	0·1	500	52
Crater Hills	4	1,021	5·45	..	400	..
Umnak Island, spring E1, 16/8/46	5	1,126	2·2	0·93	1,100	4
21/6/47	5	1,104	1·5	n.f.	1,600	..
spring H1	5	482	3·8	n.f.	270	..
Kamchatka, Nalachevskie, No. 1	6	1,595	5·85	0·55	600	17
Uzonskie, No. 4	6	1,394	40	0·23	75	280
Pauzhetskie, No. 1	6	1,713	0·8	..	4,500	..
Iceland, Haukadalur	7	126	0·06	..	4,400	..

*Per cent in mud; sample collected 3 months after water.

References 1: Brannock *et al.*, 1948; 2: White and Brannock, 1950; 3: White, 1957; 4: Gooch and Whitfield, 1888; 5: Byers and Brannock, 1949; 6: Piip, 1937; 7: G. Bodvarsson, pers. comm. to A. J. Ellis.

recently come into operation. (Cessation of deposition at a deeper level could also account for the observed change.) Two Umnak analyses in Table 5 refer to one spring sampled at an interval of a year and are suggestive in the light of what has been said above.

Evidently the antimony content of a thermal spring water may be subject to rapid and wide fluctuation and no significance can be attached to it. The present results in Table 1 show no correlation with either the arsenic or chloride content; they are consistent with a magmatic origin of the antimony and a history complicated by deposition and reworking.

The results in Table 4 show complete absence of arsenic and antimony from calcite crystallised from Wairakei bore water. Antimony is enriched relative to arsenic in the siliceous deposits from that water and in the precipitates, mainly silica, from Ohaki and Champagne Pool, Waiotapu (Table 1); also in the siliceous mud from Spring 27, Steamboat Springs (Table 5). The silica/antimony ratio is the same in the silica deposited from the Wairakei bore water and in the water itself.

The overseas analyses in Table 5, except that from Iceland, refer to the volcanic areas about the Pacific borders and the chloride/arsenic and arsenic/antimony ratios fall in the same range as those for New Zealand. For comparison with the present results, the arsenic v. chloride relations of Table 5 are included in Fig. 1. (Onishi and Sandell (1955) showed that there is no relationship between arsenic and chloride in the Yellowstone and Steamboat springs as a whole.) They are seen to fall into a pattern quite different from that given by the New Zealand waters. A tendency for the overseas waters to have a lower chloride/arsenic ratio, which would be emphasised if more of the Yellowstone Park analyses were included, is pointed out; but, in the absence of any standard for intercomparison of the analyses, it is idle to suggest explanations.

Champagne Pool, Waiotapu, and Uzonskie stand out as having exceptionally low concentrations of antimony relative to arsenic. In some of the spring waters, e.g., Ohaki, Umnak, antimony reaches concentrations surprisingly high in view of the readiness with which it precipitates, with silica, for example.

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SPONTANEOUS IGNITION OF SPENT BREWING GRAINS

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Summary

An investigation has been made of the hazards of spontaneous ignition in dry spent brewing grains. It is shown that although dry malted barley grains fail to undergo appreciable exothermic reaction with oxygen at 100°C before the malt has been extracted, dry spent brewing grains exhibit a vigorous exothermic reaction. This reaction is caused by the presence of the natural oil in the grains. The heat output of the reaction between a selected sample of dry spent brewing grains and dry air has been measured over the range 35° to 90°C, and the results are used to predict the spontaneous ignition hazard of various sized piles of this dry material over the experimental temperature range. It is shown that within this range the external restrictions to heat flow that are likely to apply to piles of material in commerce would have only a small influence on the critical state. An approximate method is suggested for calculating the thermal stability of a stack of bagged grains.

INTRODUCTION

The spent barley grains from which malt has been extracted to brew beer are normally sold for use as animal feeding stuffs. Sometimes they are sold wet and used directly as feed for stock, with obvious difficulties in transport and storage. Alternatively the spent grains are dried, yielding a product with good keeping qualities. These dried grains are then either used directly as fodder, or incorporated in formulations for stock food. When dried spent brewing grains are stored in large quantities, spontaneous fires sometimes occur. Arms (1930) describes a fire of spontaneous origin in a bin of distillers grains (i.e., spent brewing grains). Beistle (1930) has stated that between 1910 and 1927 there were 40 outbreaks of fire or spontaneous heating in dried distillers grains whilst in transport on American railroads. Moulton (1948) rates the spontaneous ignition hazards of over-dried spent brewing grains as "very dangerous", and recommends that the moisture content should be maintained between 7% and 10%, and that the grains should be cooled below 100°F (38°C) before storage. The Board of Underwriters of New York (via Thomas, 1957) classifies dried spent brewing grains as a hazardous cargo, and recommends dry stowage. More recently the Bureau of Fire Mobilisation and Control (1952) has drawn attention to the frequency of spontaneous fires in dried brewing grains, and has expressed the opinion that spontaneous heating to ignition temperatures will occur if grains are dried to less than 7% moisture content. The Fire Protection Association (1957) has warned that spent brewing grains are prone to spontaneous heating if dried to a moisture content of 5% or lower. Several fires have occurred in New Zealand through spontaneous ignition of dried spent brewing grains.

To investigate a spontaneous ignition problem of this type, two different experimental approaches are conventionally available. One is to expose samples of the material to standardised laboratory test conditions (with ambient conditions maintained either isothermal or adiabatic) and see if there is any tendency to ignition, and then to make comparisons between behaviour in such a test and the behaviour of the same materials under practical storage conditions. The other approach is to measure the kinetics of reaction between air and the material under investigation, and then use this data along with other physical constants to predict the ignition hazards of the material when stored in large masses. The first method (application of various standardised ignition tests) has been applied by various investigators to a wide range of problems. It offers a number of advantages. It can provide positive correlation with practical storage experience. The experimental simplicity of most standardised tests facilitates examination of samples from many different sources, and it is convincing to have actual fires demonstrated in the laboratory. Many chemical reactions have a reaction order greater than zero, and reaction rate therefore decreases during the course of a standardised test as reactant becomes consumed in the heating reaction. By wise choice of the quantity of material involved in the test it is possible to make some allowance for this effect, and to devise a test which expends the greater part of the primary reactant in attaining ignition temperatures. A well designed standardised test with isothermal ambient temperature is ideal for proving that a given material is safe in storage, since conditions can be made more severe than normal (e.g., elevated temperatures and/or increased oxygen partial pressure). However, with a material that gives intermediate results in a test of this type it is difficult to evaluate the storage hazards, especially if a wide range of correlation is not available between test results and storage experience. And this type of correlation is not easy to obtain, since material salvaged from fires is frequently modified in its chemical properties. The second experimental method (measurement of reaction kinetics) also offers advantages. By mathematical interpretation it is possible to make reasonably accurate predictions of storage behaviour over the temperature ranges covered by experiment, and this avoids the necessity (although not the desirability) for correlation with practical storage experience. A further point is that conditions of temperature and oxygen partial pressure in laboratory experiments can be kept closer to those applying in commerce than it would be convenient to use in standardised ignition tests. Disadvantages are first, that the complexity of kinetic measurements creates difficulties in examining a wide range of samples, and next, that all existing mathematical interpretations of kinetic data to predict storage behaviour are limited to reactions of zero order (Walker, 1961). A simplification sometimes suggested is an assumption that the initial stages of a first order reaction are equivalent to zero order, since a negligible amount of reactant has been expended. This is not true in practice, since a first order reaction diminishes at the same relative rate throughout its life. In point of fact, the late stages of a second (or higher) order reaction are much more like zero order than is any stage of a first order reaction. Many authors have further failed to draw a distinction between the contributions to reaction order of the gas phase, and of the solid (or liquid) phase. Even if the simplification is made that air diffusion into the mass is

sufficient to hold oxygen concentration reasonably constant, it might be doubted if spontaneous ignition reactions are commonly zero order. Walker (1961) has shown that if the reaction order is greater than zero, all existing mathematical treatments of thermal instability must be applied to a specific early stage in the reaction, and that this early stage represents the maximum ignition hazard.

It was therefore decided to approach the problem of investigating the hazards of spontaneous ignition of dry spent brewing grains by studying the reaction kinetics of a single sample in detail to enable estimation of the storage hazard in various volumes, and also to apply a simple ignition test to a range of samples to see if this sample selected for kinetic study is representative of the material as a class. In each of these experiments the quantities of heat under measurement were small in comparison with the heat that could be involved in evaporation or condensation of any water present in the system, so, before starting each experiment, all moisture was eliminated from the sample. For measurement of oxidation kinetics of materials of low thermal conductivity, various forms of calorimeter have been designed. The design of Walker and Harrison (1960) was chosen since it combines sensitivity with simplicity, and is not limited to operation at one specific temperature. This calorimeter produces results in the form of a ratio of reaction rate (per unit volume) to thermal conductivity, and reaction rate cannot be established as a separate parameter without knowledge of the values of density and thermal conductivity. Although Walker and Harrison (1960) and Walker (1961) have shown that this need not handicap interpretation of the experimental results in terms of spontaneous ignition hazard, it was thought desirable also to know reaction rate as a separate parameter, to facilitate comparisons with other materials. Density of the dry grains is easily determined, but thermal conductivity is not an easy measurement. Conventional methods of measurement are not suited for application to natural products having an appreciable equilibrium water content, and are certainly not suited to a material that reacts with air to produce heat. Thermal conductivity and its variations with temperature depend so much on the state of subdivision of the material and on its admixture with other materials such as water or oils, etc., that they are difficult to predict for any unknown material from comparisons with known materials.

However, a physical property exists that is related to thermal conductivity in a simple manner, and that can be predicted with reasonable accuracy for any material. Joule's law states that the specific heat of any solid material approximates to the sum of the atomic heats of its constituents, and Partington (1952) has reviewed the applications of this law and the exceptions found to it in practice. This review shows that the specific heat of any organic solid natural product could be determined reasonably accurately from the results of analyses, and from comparisons with the specific heats of other similar materials. Specific heat is related to thermal conductivity by the theory of thermal diffusion, and Ingersoll *et al.* (1948) have summarised tabulated functions enabling calculation of the thermal diffusivity of a material from the central temperature changes caused by application of a sudden change in surface temperature. The spherical calorimeter vessels employed by Walker and Harrison (1960) are well suited to such an experi-

ment, and also enable the effects of moisture content and of exothermic reaction with air to be controlled. In this way approximate values of thermal conductivity can be found for the sample under investigation, over the relevant range of temperature, without adding to the experimental complexity.

EXPERIMENTAL

The sample of spent brewing grains selected for kinetic studies had already been dried under commercial conditions (screw press, followed by steam heated drum drier). This sample was thoroughly mixed before use, and stored at normal air temperatures in polyethylene bags for 110 days whilst the kinetic experiments were being carried out. Five other samples of similarly dried spent grain were taken from the same drying process, representing different batches of brewing grains originating from different breweries. In addition, five samples of wet spent grains representing different types of malted barley were obtained direct from the brewing process, and these were centrifuged and then dried for three days in shallow layers (1 cm) in air at 35°C. In the case of two of these samples, samples of the parent malted grains were also obtained.

The standardised ignition test employed is as described by Walker and Williamson (1957) i.e., oxygen at 100°C. The actual volume of flask used was 2,220 ml. The various samples tested had different bulk densities, so instead of using a fixed weight of sample, the flask was filled with air-dry grains and the weight noted in each experiment. The dry bulk density in the reaction flask was then calculated from a moisture content determined separately by conventional oven drying to "constant" (i.e., minimum) weight (105°C).

The calorimeter used was identical with the design of Walker and Harrison (1960) except that instead of drawing the central thermojunction into position after filling the flask with sample, it was held centred by a taut nichrome wire of 0·011 in. diameter to which it was soldered. The spent brewing grain was then poured into the flask, and gently packed to a convenient standard density sufficient to avoid shrinkage during the experiment. All other experimental procedure was identical with that described by Walker and Harrison (1960). The calorimeter experiments at various temperatures were carried out in a random sequence over the 110 day period, to avoid any possibility of changes during storage having a systematic influence on the results. Analyses of exit gases from the calorimeter vessel confirmed that ventilation rates were adequate to prevent the oxygen content dropping below 20% in any experiment.

The thermal diffusion experiments were carried out with one of the standard (5 l) calorimeter flasks after the oxidation experiment had been completed. The ventilating gas used was nitrogen (containing about 50 p.p.m. oxygen) to avoid oxidation heating, and was passed at a rate of 25 ml/min to minimise heat loss in the gas stream. To further minimise heat loss, the central thermocouple was made from 0·011 in. diameter constantan and 0·006 in. diameter copper wires. The flask of grain was brought to a uniform temperature in a thermostatically controlled

water bath (± 0·02°C), and cold water was suddenly flowed in to drop the temperature about 18°C in about 2 minutes. The thermostat was then controlled at the lower temperature, and observations made of the times at which the central temperature in the flask reached preselected values representing $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the external temperature drop.

In the experiments reported in Tables 2 and 3 the thermometers and thermocouples used were calibrated against NPL certified thermometers.

RESULTS

In Table 1 are shown the "fat" analyses (diethyl ether extract) of the various samples, together with the temperature rises (i.e., rises above 100°C) obtained in the standardised ignition test (Walker and Williamson, 1957). The temperatures marked "plus" showed signs of rising indefinitely (cf Walker and Williamson, 1957), and the incipient fires were quenched by readmission of CO_2. Some of these samples exhibited a central carbonised core which glowed in air when emptied from the flask immediately after testing. To discover the effects of using dry air instead of dry oxygen in Walker and Williamson's test (1957), a portion of the "standard" sample K (0·23 g/ml) was tested in dry air, and rose 21°C in 7½ hours. Also included in Table 1 is a test on the "standard" sample (K) after it had been extracted with ether in a Soxhlet apparatus. Some of the oil extracted from this spent grain was dissolved in a mixture of diethyl ether and petroleum ether (BP $<$ 40°C) and spread uniformly over acetone-extracted wool (29·4 μ diameter at 50% RH) and the solvent evaporated (cf Walker and Harrison, 1961.) This oily wool was then subjected to ignition test (Walker and Williamson, 1957).

In Table 2 are shown the peak temperature differences measured between centre and perimeter of the spherical calorimeter vessels (Walker and Harrison, 1960) together with relevant experimental data. Also shown are the temperatures measured after elapse of the time interval specified by equation (2) (see below). Fig. 1 shows typical time/temperature curves obtained in this apparatus.

In Table 3 are shown the times taken to attain various temperatures at the centre of the spherical flask packed with grain to a dry density of 0·271 g/ml, after suddenly lowering the external temperature. The spent grain was perfectly dry when tested, so by assuming a specific heat of 0·5 (cal/g/°C) for the oil present, and 0·37 for the remainder of the grain, a figure of 0·38 is obtained for specific heat. Table 3 shows values of thermal conductivity calculated by substitution of this value in the numerical data presented by Ingersoll *et al.* (1948). Preliminary experiments using both 5 l and 10 l flasks with thermocouples of 0·011 in. diameter copper/constantan wire yielded thermal conductivity values in both cases about 7% higher than those here presented, with a difference between the 25%, 50%, and 75% points slightly greater than in the present experiments. These variations were probably due to the increased thermal conductivity of the thicker copper thermocouple wires.

TABLE 1—Ignition Testing and Analysis of Brewing Grains

Sample Designation	Description	Drying Process	Ether Extract (% on Dry Weight)	Dry Bulk Density (g/ml)	Ignition Tests (Oxygen at 100°c) Maximum Temp. Rise (°c)	Ignition Tests (Oxygen at 100°c) Time to Reach Max. Temp. (hr)
A	Whole malted barley	..	1·9	0·54	1	55·2
A	Crushed malted barley	..	1·6	0·43	3	15·8
A	Spent brewing grain	Laboratory	8·0	0·17	37	5·3
B	Whole malted barley	..	1·8	0·59	2	15·5
B	Spent brewing grain	Laboratory	6·9	0·20	44	5·9
C	Spent brewing grain	Laboratory	9·4	0·20	128 plus	3·5
D	Spent brewing grain	Laboratory	7·8	0·20	51	5·7
E	Spent brewing grain	Laboratory	7·5	0·20	51	5·8
F	Spent brewing grain	Commercial	9·3	0·24	60	5·7
G	Spent brewing grain	Commercial	8·3	0·25	69	7·8
H	Spent brewing grain	Commercial	9·3	0·26	136 plus	5·4
I	Spent brewing grain	Commercial	9·3	0·26	59	8·8
J	Spent brewing grain	Commercial	8·8	0·26	105 plus	7·8
K	SBG standard sample	Commercial	9·3	0·23	77	5·8
K	SBG standard sample	Commercial	9·3	0·23	63	7·3
K	SBG standard sample	Commercial	9·3	0·24	124 plus	4·9
K	SBG standard sample	Commercial	9·3	0·25	157 plus	5·8
K	SBG standard sample	Commercial	9·3	0·24	70	6·9
K	SBG, standard sample after extraction with ether	..	0	0·21	2	6·3
..	Oil from K, spread on wool	..	11·7	0·081	"Fired"	1·23
..	Oil from K, spread on wool	..	11·7	0·081	"Fired"	1·23

TABLE 2—Central Temperature Rises in Spherical Flasks of Dry Spent Brewing Grains in Dry Air

Bath Temperature (°C)	Flask Volume (ml)	Grain Density (dry) (g/ml)	Air Flow Rate (ml/sec)	Peak Temperature Rise (°C)	At Time shown by Equation (2)	
					Time Delay (hr)	Temperature Rise (°C)
87·08	1015	0·271	3·3	3·06	13·6	3·06
84·44	1015	0·271	3·3	2·57	16·0	2·57
80·86	1015	0·271	3·3	1·87	20·0	1·87
79·76	2240	0·268	3·3	4·23	20·0	4·15
77·65	1015	0·271	3·3	1·71	24·0	1·71
68·01	2240	0·271	3·3	2·18	40·8	1·92
62·74	5270	0·255	6·7	2·42	54·2	2·34
57·48	5260	0·271	4·0	1·72	74·1	1·65
52·25	5270	0·271	3·3	1·16	101	1·15
52·25	5270	0·271	3·3	1·20	101	1·16
41·84	10,430	0·271	5·0	1·14	180	1·14
34·24	10,430	0·271	3·3	0·63	279	0·63

TABLE 3—Thermal Diffusion in a Spherical Flask of Dry Spent Brewing Grain

(Sample "K," 0·271 g/ml, radius = 10·8 cm)

Central Temperature Change (%)	Selected Central Temperature (°C)	Measured Elapsed Time (min)	Calculated Thermal Conductivity (10^{-4} cal/sec/sq cm/cm/°C)
0	97·43	0	..
25	93·34	92	2·02
50	89·25	153	1·83
75	85·16	249	1·70
100	81·07	..	..
0	81·07	0	..
25	76·47	97	1·92
50	71·87	152	1·84
75	67·27	240	1·76
100	62·67	..	..
0	62·67	0	..
25	58·11	101	1·85
50	53·54	155	1·80
75	48·98	237	1·78
100	44·42	..	..
0	57·65	0	..
25	53·06	100	1·85
50	48·47	154	1·82
75	43·88	235	1·80
100	39·29	..	..

DISCUSSION

The results in Table 1 show that whilst samples of dry malted barley grain have little tendency towards exothermic reaction with oxygen at 100°C, either whole or crushed, the dried samples of spent grain remaining after aqueous extraction of malt in the brewing process show a vigorous reaction. In these reactions there was marked evidence of an induction period. The analyses show that fat content is much higher in the spent grain. This is an obvious result of the mashing process (Hind, 1940) since hot aqueous extraction considerably reduces the total weight of the crushed malted barley, but is unlikely to remove much of the natural oils. Moreover, it is likely that degradation of the cereal grain and the subsequent hot water treatment would cause any oil present to be spread more uniformly through the residual material. Typical fat analyses of spent grain on a dry weight basis are 6·4% (Bishop, 1934, *via* Hind, 1938) and 5·1% (Preece, 1954), showing that the present samples are not abnormally high in fat content. There appears to be little correlation between the fat content of the spent grain and behaviour in the ignition test. There also appears to be no systematic differences between ignition tests on the samples of grain dried under laboratory conditions and those dried under commercial conditions. No relationship was found between the variations in replicate tests, and the time the standard sample had been held in storage at room temperatures.

Thompson (1927) has pointed out that the Mackey test for spontaneous ignition divides oils sharply into two classes although no such division exists in practice. Thompson (1927, 1928) described experiments using other standardised test conditions which showed a similar division, and demonstrated that by changing the test conditions this point of sharp division would vary. Walker and Harrison (1961) considered that Walker and Williamson's test (1957) would probably also impose a sharp artificial division on samples of pie wool. From the interpretation of spontaneous ignition presented by Walker (1961) it can be seen that the maximum temperature attained in a test of this type will be controlled by the temperature coefficient as well as rate of reaction; and order of reaction will also exert an influence on the course of the heating. The results for sample K in Table 1 suggest that the test is operating to give an undesirably sharp discrimination in the present experiments, and if so, a comparison could be drawn with the experiments using 5·6% oleic acid spread on wool described by Walker and Harrison (1961). This may explain the apparently wide differences between ignition test results shown in Table 1. The experiment in which the standard test was carried out using air in place of oxygen may be compared with similar experiments on pie wool described by Walker and Harrison (1961), and has yielded a comparable reduction in reaction rate.

The experiment in which the spent grain was extracted with ether before test demonstrates that the exothermic reaction with oxygen is caused by the oil content, since removal of oil has prevented the reaction (Table 1). This was confirmed by spreading the extracted oil on wool, when the tests showed a vigorous reaction (Table 1), quite comparable with that caused by oleic acid spread on wool and exposed to the same test conditions (Walker and Harrison, 1961). The exothermic reaction with oxygen is thus caused by the seed oils exposed on the large surface of the spent grains. It is relevant to note that Moulton (1948) gives dried spent brewing grains the same rating for spontaneous ignition hazards whether or not the oil has been removed. It is possible that grains with the oil removed could heat by microbiological activity if they were too damp, but it is unlikely that such heating would lead to fire. And if the oil were efficiently removed, the present experiments show that there would be no fire hazard at moisture contents below 7%.

The present technique of measuring thermal diffusivity and deducing thermal conductivity by assuming a value for specific heat, appears capable of yielding results of adequate accuracy. It is unlikely that the value for specific heat is in doubt by say 20%, and the thermal diffusion results for the 25%, 50%, and 75% temperature change points are sufficiently well in agreement to inspire confidence in the method. The final value of thermal conductivity should be at least within $\pm$ 20% of the true value, which is adequate for the present purpose. This technique appears to have been first applied (for a measured value of specific heat) by Aryton and Perry (1878), and should find wider application to the measurement of thermal conductivity of materials. In particular it should be of value for mixtures such as a fibrous solid with a liquid (e.g., a textile fibre plus water and/or oil) for which specific heats of the individual components are known.

In interpretation of the calorimeter experiments, the first problem arising is that of finding an equivalent stage in the reaction, so a comparison can

be made between calorimeter experiments at different temperatures. It can be seen from Fig. 1 that the temperature in each experiment takes a long time to rise to a maximum, and then falls. The time taken for a sphere of a material generating heat at a constant rate to attain a stable tempera-

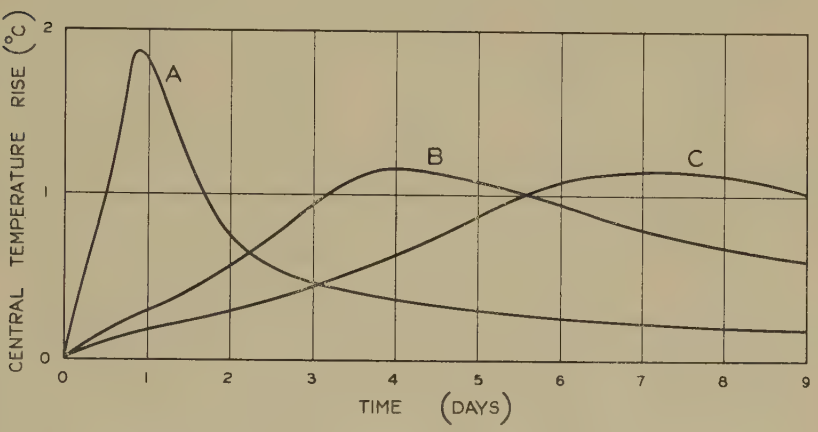

FIG. 1—Typical self-heating of spent brewing grains in dry air:
A 1 l flask at 80·86°C.
B 5 l flask at 52·25°C.
C 10 l flask at 41·84°C.

ture distribution can be calculated (Carslaw and Jaeger, 1959), and application of the present parameters shows that at this constant rate of reaction the present 1 l flasks could be expected to attain 90% of the final temperature rise in 2 hours, and the 10 l flasks in 7 hours. The curves of Fig. 1 show that experimental peak temperatures are attained much more slowly than this, and suggest that the reaction has an induction period. The subsequent fall in temperature demonstrates that the order of the oxidation reaction (once begun) is greater than zero with respect to the reacting oil. Equivalent points in an oxidation reaction at a series of temperatures can be found by making measurements in each experiment when the reaction has proceeded to an equivalent stage. Walker and Harrison (1960) suggested that at each temperature an equivalent stage could be found by using the finally determined temperature coefficient to calculate the time the reaction is permitted to proceed before the reading is taken, arbitrarily selecting a convenient stage in the reaction for this purpose. However, the pie wool reaction that Walker and Harrison (1960) were investigating did not show any appreciable induction period.

Henderson and Young (1942) investigated the kinetics of oxygen absorption by pure oleic acid, and found a marked induction period. They worked at a fixed temperature (80°C), and varied conditions of oxygen partial pressure over the range 21% to 99·5% oxygen (at 760 mm pressure). Henderson and Young (1942) measured the rate of absorption of oxygen,

and found a reaction order of $n = \frac{1}{2}$ with respect to oxygen partial pressure, but claimed that the induction period was unaffected by change of oxygen partial pressure over this range. This must mean that the chemistry of the induction period was of an order approaching zero with respect to oxygen concentration over this range of oxygen partial pressures. Henderson and Young (1942) chose an equivalent point to compare different experiments by measuring the rate of oxygen absorption at an arbitrarily chosen point where 0·1 mole of O_2 had been absorbed per mole of oleic acid. In graphing their experimental curves they shifted them along the time axis to compensate for differences in induction period between experiments. In the present experiments it is obvious that the duration of the induction period is not independent of temperature. As can be seen from Fig. 1 the reactions at lower temperatures take a longer time to reach a peak reaction rate than do reactions at higher temperatures. Investigators of oxidation reactions in unsaturated fats have paid little attention to the kinetics of the induction period, but there is no *a priori* reason to assume that the kinetics of the induction period are the same as the kinetics of the main reaction, since it is reasonable to think that the chemistry is different in the two cases. However, as will be demonstrated, experiments show that in the present case the temperature coefficient of the induction period is very close in value to the temperature coefficient of the main oxidation reaction.

By following the calculation procedure suggested by Walker and Harrison (1960), the results of Table 2 were used to compute values of $\frac{\rho Z}{k}$ at various temperatures, and these are shown in Fig. 2 (corrected to a common density of 0·271 g/ml). Table 2 gives values for ρ and Table 3 values for k (here concluded to be $1{\cdot}8 \times 10^{-4}$ cal/sec/sq. cm./cm/°C at all experimental temperatures), and substitution of these values yields values of reaction rate (Z), also shown in Fig. 2. Table 2 and Fig. 2 include all experiments made in the present investigation. The scatter of the data is such that there is little to choose between a straight line plot of log Z against T, or a plot against the more conventional $\frac{1}{T}$. In view of the use of a fixed value of y in the Walker and Harrison (1960) calculation method, and of the greater simplicity of Walker's (1961) method of calculating the critical state in comparison with Frank-Kamenetskiĭ's equation (1939, 1942), reaction rate was plotted directly against temperature on a log linear scale. Fig. 2 shows that over the temperature range 35° to 90°C the rate of reaction doubles for a rise of 12·4°C. At any temperature τ°C between 35° and 90°C the rate of reaction is expressed by

$$Z \text{ (cal/sec/g)} = 2{\cdot}15 \times 10^{-6} \cdot 2^{0{\cdot}0806\tau} \qquad \text{.....(1)}$$

This same temperature coefficient can be used to determine the time delay at each temperature before the temperature rise is measured. Since the time constant of the rate of change of reaction velocity is reasonably long in each experiment compared with the time constant for heating of the grain (Carslaw and Jaeger, 1959), any point on the curves of Fig. 1 could be considered sufficiently stabilised for measurement of the temperature rise. How-

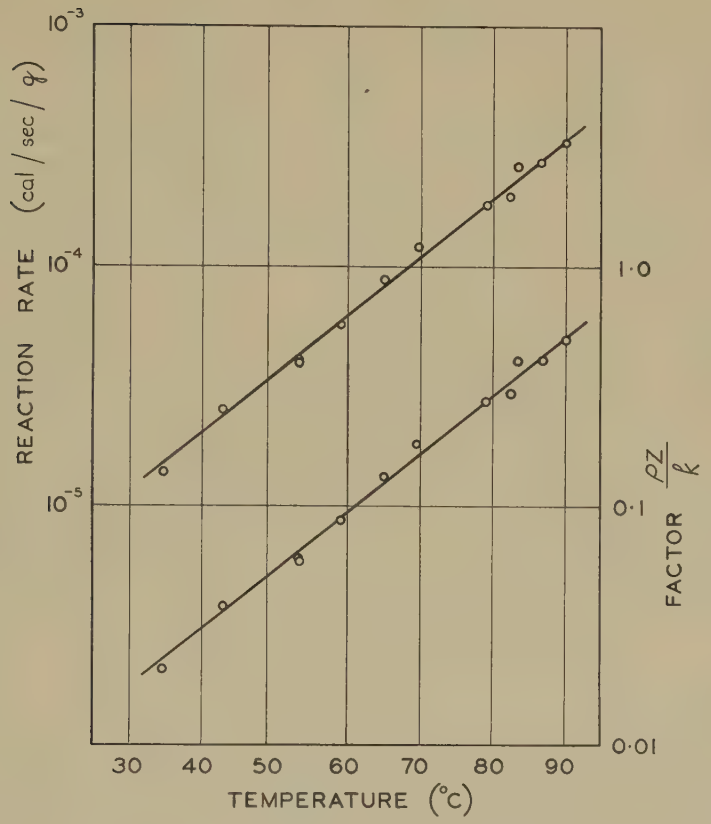

FIG. 2—Rate of reaction of dry spent brewing grains in dry air.

ever, the most convenient point is one very slightly after the peak temperature rise in each case, since this represents a maximum hazard, and avoids the influence of any irregularities in the induction period. Such a point is found to be,

$$\text{Time (hr)} = 1925 \times 2^{-0{\cdot}0806\tau} \qquad \ldots\ldots\ldots\ldots (2)$$

For this last purpose, τ is taken as the arithmetic mean of the stabilised central and surface temperatures in the reaction flask. When equation (2) is applied in this manner it is found that measurement of temperature rise is being made in each case at or a little after the time of peak temperature rise. The fact that time delays in each experiment computed in accordance with equation (2) roughly coincide with peak temperatures measured in each case, demonstrates that the temperature coefficient of the induction period is about the same as the temperature coefficient of the main heat liberation reaction. This is confirmed by Fig. 3, which shows a plot of all experimental temperature rises. Fig. 3 has been drawn by multiplying all experimental times by $2^{0{\cdot}0806\tau}$ to provide a common basis for comparison. (The time delay corresponding to equation (2) is shown dotted in Fig. 3).

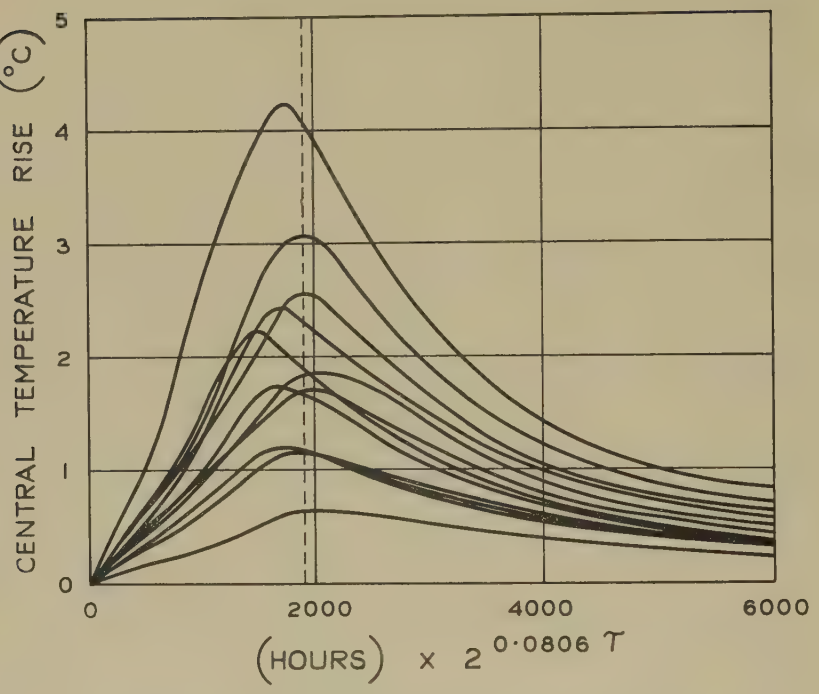

FIG. 3—Experimental calorimeter curves reduced to a common time scale.

There exists another fat oxidation reaction that appears to have a temperature coefficient for its induction period identical with that of the final reaction rate. Gunstone and Hilditch (1945) investigated the rate of peroxide formation of pure methyl oleate exposed to pure oxygen, and reported induction periods and rates of peroxidation over the range 20° to 130°C. Calculations based on their published data show that over the temperature range 50° to 100°C the induction period and the final rate of peroxide formation have practically identical temperature coefficients, corresponding to the reaction rate doubling (or the induction period halving) for each temperature increase of 9·2°C over this range. It therefore seems that kinetics of the induction period of fat oxidation reactions would repay further study, as this might throw some light on the chemistry of the induction period.

As discussed above, it is likely that Walker and Williamson's test (1957) is exercising a high degree of discrimination on the present samples, and samples of the same reactivity are seen to range between a temperature rise of about 60°C and over 120°C (cf Walker and Harrison, 1961). In light of this, the results of Table 1 show that the material chosen for kinetic study is reasonably typical of the spent brewing grain commercially available in New Zealand, and enable deductions of the ignition hazard in commerce to be made from the kinetic data with confidence. When a large pile of dry

spent brewing grains is assembled, the porous nature of the material will permit reasonable access of atmospheric oxygen to the interior. Reaction with this oxygen liberates heat, and a thermally unstable state can be produced in which the central temperature can rise indefinitely (Frank-Kamenetskiĭ, 1939). The data shown in Fig. 2 enable calculation of the sizes of various shaped piles of a material identical with that used in the present calorimetric measurements, which would attain a "critical state", i.e., the threshold of spontaneous ignition. Commercial piles are likely to approximate to spheres or cylindrical silos, and in Fig. 4 are shown the

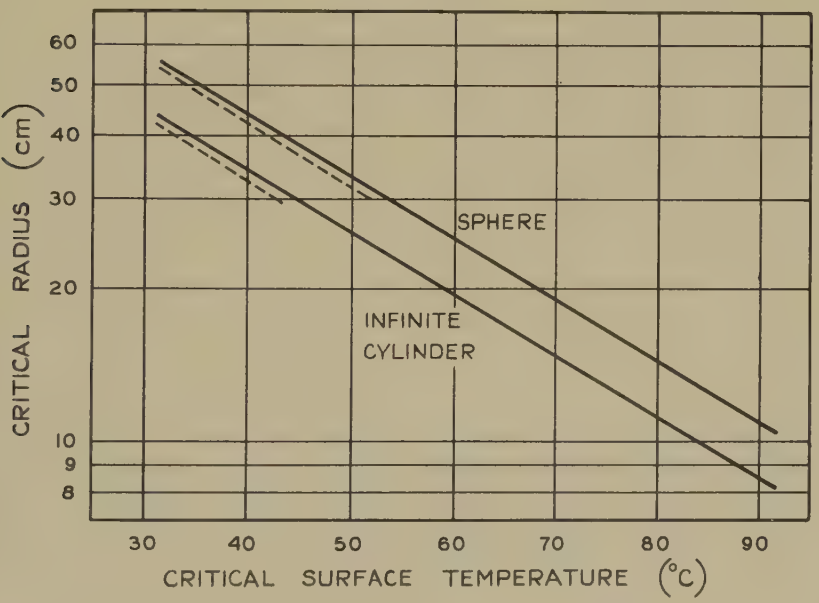

FIG. 4—Thermal instability in piles of dry spent brewing grains in dry air.

relationships between critical radius and critical surface temperature for spheres, and for cylinders of effectively infinite length, with surfaces perfectly cooled to ambient temperature, for dry spent brewing grain identical to the material used in the calorimetric experiments. These figures are plotted on a log linear scale for convenience, and are calculated from the formulae proposed by Walker (1961). Piles with surface temperatures below the critical temperatures shown in Fig. 4 would not ignite, although the internal temperature would rise. For instance, if the surface temperature of each size of pile in Fig. 4 were lowered by about 20°C, the pile would be completely free from risks of ignition (Walker, 1961). In the case of stored piles of cubical shape, the data of Fig. 4 can be applied directly by equating them to spheres of radius 16% greater than the actual half-thickness (Walker, 1961). Walker (1961) has also proposed a method for calculating the critical ambient temperature for symmetrical piles having limited thermal

conductivity to the nearest heat sink. In the present case of dried spent brewing grains this restricted conductivity would be more likely to take the form of an interposed inert material than a surface heat transfer coefficient, and a likely extreme case might be a thermal barrier consisting of a 6-in. thick concrete wall. Such a wall might be used to contain piles of radius, say 30 cm or more, and would provide a surface thermal conductivity of about $1{\cdot}5 \times 10^{-4}$ cal/sec/sq cm/°C. Calculations (Walker, 1961) show that this concrete containing wall would cause the critical ambient temperature for a 30 cm radius pile (sphere or cylinder) to be about 2°C lower than the critical surface temperatures shown in Fig. 4, and this difference would be less for larger piles. These corresponding critical ambient temperatures are shown dotted in Fig. 4.

One method sometimes used commercially to avoid the ignition hazards of large piles is to fill individual sacks with the material, and build a stack of sacks. The problem of evaluating the ignition hazards of such a stack has not yet been solved mathematically. However, the above demonstration of the minor effect that restricted surface cooling has on critical ambient temperature for the piles of Fig. 4 suggests a method that could be used to treat such a stack. As Walker (1961) has shown, the total heat released in a spherical or cylindrical pile in the critical state is not more than twice the heat that would be released by the same pile reacting uniformly at the ambient temperature. If a surface heat transfer coefficient of 5×10^{-4} cal/sec/sq cm/°C is assumed, this means that minor air movements within the stack will suffice to remove the heat liberated at the exposed surfaces. The stack can thus be regarded as a lattice of interlaced cylinders (each of effectively infinite length), and each of cross section about four times the average area of contact between bags. To allow for the effects of the cylinders interlacing, a radius can be assumed perhaps four times that represented by the contact circles. This will suffice to approximate the stack to a single cylinder, and the problem can then be solved from the data of Fig. 4. Such a treatment explains why individual bagging is so effective in preventing spontaneous ignition in a large stack.

Deductions regarding storage behaviour at other temperatures cannot be made from the data of Fig. 4, since it is not safe to extrapolate data outside the limits at which experimental measurements have been made. The material ether-extracted from the present spent brewing grains was liquid at room temperature and there is therefore no particular reason to suspect that the temperature coefficient of the oxidation reaction would be anomalous at temperatures between 35°C and room temperature. However, experience with storage behaviour at room temperature provides some evidence of the rate of oxidation at lower temperatures, and 110 days storage of the present standard sample (K) at temperatures varying between 10° and 20°C failed to show any appreciable effect on the ignition tests and calorimetric experiments. Equation (2) suggests that a maximum of 60 days at these temperatures should complete the induction period and bring heat generation to a peak rate. Since the present experiments showed no evidence of correlation with age during 110 days storage, this must mean either that the temperature coefficient was anomalous at low temperatures, or that the reaction during storage was inhibited by the presence of equilibrium moisture (13·4% on

dry weight in the present case). However, the data presented by Gunstone and Hilditch (1945) show that the temperature coefficient of peroxidation of pure methyl oleate is anomalous between 20° and 50°C, and exemplify the errors that might be incurred by extrapolation of experimental data to predict oxidation rates of unsaturated fats, particularly when induction periods are involved.

The present experiments still leave the role of water in the oxidation reaction in some doubt. Spent brewing grains normally contain about 11% water by weight (Preece, 1954), and the present standard sample of grain contained 13·4% (on the dry weight) in an air-dry condition. Various authorities have considered (Bureau of Fire Mobilisation and Control, 1952; Fire Protection Association, 1957) that drying spent brewing grain to moisture contents less than 7% or 5% would increase the risks of spontaneous ignition. It is not clear what experimental evidence or experience this view is based on. The suggestion is made (Bureau of Fire Mobilisation and Control, 1952) that severe drying may cause oxidation of the oil; and Van Elteren (1958) has described experiments on textile oleines that show how such oxidation can increase fire hazard by completing the induction period of an oil, and so raising the reaction rate. Severe drying can have other effects also. The over-dried grains will reabsorb water from the atmosphere during subsequent storage, and so liberate the latent heat of vaporisation. Moreover, if material that is in perfect moisture equilibrium with the atmosphere begins to self-heat, it will tend to evaporate moisture into the ventilating air, and so oppose the heating. This effect will not operate with over-dried grains. A further point is that material badly over-dried is perhaps more likely to be binned whilst still hot from the drier, as indicating careless operation of the process. There is some doubt about what effect the presence of equilibrium water might be expected to have on the rate of oxidation of an unsaturated fat. Thompson (1928), Ellis (1936), and Van Elteren (1958) have studied reactions of this type, and all consider that water would have little or no inhibiting effect. However, Walker and Harrison (1961) studied the effect of moisture on the reaction between pie wool and oxygen, and concluded that the rate of oxidation is definitely inhibited by the presence of moisture. The present failure to notice any change in the standard sample during a 110-day storage period at room temperatures may possibly be due to the inhibitive effects of equilibrium moisture content. Summing up, it is likely that overdrying spent brewing grain could promote subsequent heating by reabsorption of equilibrium moisture during storage, and could cause the oxidation reaction to have a shorter subsequent induction period, and to proceed more vigorously. The present experiments based on perfectly dry spent brewing grains therefore represent a maximum hazard. Whilst it is probably unwise to overdry spent brewing grains, it is certainly dangerous to build piles at temperatures approaching within say 20°C of those corresponding to the sizes shown in Fig. 4.

The Bureau of Fire Mobilisation and Control (1952) also recognises that spent brewing grains that contain too much moisture may heat due to fermentation. To this must be added the hazards of heating due to the metabolism of moulds, if the material contains sufficient moisture to produce

a relative humidity in excess of 75% in the interstitial atmosphere. This recognition of the possibility of self-heating by mould activity follows from demonstrations by Carlyle and Norman (1941) and Milner *et al.* (1947) that mould activity can cause temperatures of up to 55°C, and from the demonstration by Galloway (1935) that moulds can metabolise actively at humidities above 75%. Such microbiological activity might well heat the material to a point where the oxidation reaction becomes of sufficient magnitude to cause thermal instability, with consequent ignition. This would be caused in a pile of dry material, for example, by any internal spherical boundary of a size represented by Fig. 4 reaching or exceeding the corresponding critical surface temperature. Even if this internal spherical boundary then become no hotter, all material contained within it would become thermally unstable, and would rise to ignition temperature (provided the reaction were not restricted from other causes, such as lack of access of oxygen). This mechanism commonly operates in large stacks of any material that is prone to spontaneous ignition, and it is not unusual to find several centres of fire in such combusting material.

The order of the present oxidation reaction has not been investigated. The oxygen concentration in the calorimetric experiments was held between 21% and 20%, so its contribution to overall reaction order is not known. Comparison with other fat oxidation reactions (Burgoyne and Thomas, 1951; Walker and Harrison, 1961) suggests that the reaction is likely to be about first order with respect to oxygen at compositions below that of air. The curves of Fig. 1 also show that the present reaction is of an order greater than zero with respect to the reacting oil. The present calculations, based on a peak of activity in each experiment and on an ample supply of air, thus represent a maximum hazard, and reacting piles in commerce are likely to be more restricted by lack of ventilation and by depletion of reactant oil. The surface temperature necessary to support a critical state in any given size of pile is therefore likely to increase steadily as the internal temperature rises (Walker, 1961).

CONCLUSIONS

1. Dry spent brewing grains will react exothermally with dry oxygen or air. The generation of heat is caused by oxidation of the natural oil present in the grains.

2. The rate of generation of heat by a selected sample of dry spent brewing grain in dry air was found to be $1{\cdot}5 \times 10^{-5}$ cal/sec/g at 35°C, and over the range 35° to 90°C the rate doubled for each rise of 12·4°C.

3. A spherical pile 51 cm in radius of the sample of dry spent brewing grain investigated, reacting with an adequate supply of dry air, would become thermally unstable at a surface temperature of 35°C. This sample is reasonably typical of dried spent grain from New Zealand breweries (when in a perfectly dry state).

4. The effect of the presence of normal equilibrium moisture content on the oxidation reaction has not been investigated, but it is likely to be inhibitive.

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NOTE ON THE DISTRIBUTION OF LARVAE OF *Chironomus novaezealandiae* HUDSON RELATIVE TO SALINITY OF THE ENVIRONMENT

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A mass outbreak of midges (*Chironomus novaezealandiae* Hudson) occurred in early 1959 in the Mangere district of Auckland. A survey of the site of the Auckland Metropolitan Drainage Board Manukau sewage purification works (then under construction) revealed large populations of Chironomid larvae (bloodworms) present in mud covered with shallow water over a substantial part of the area.

Most of the works site had been reclaimed from the Manukau Harbour and when this survey was carried out during May 1959, a variety of ecological environments of different salinity were present ranging from fresh water to concentrated sea water. Midge breeding was quite sharply confined to situations of low salinity or fresh water.

A number of water samples (27) were taken over the area and subsequently analysed for salt content (by conductivity measurement) and chloride content (by Volhard titration). The results of these analyses (expressed in both cases as percent sodium chloride) where midges were breeding are summarised in Fig. 1.

Total salt content of the samples ranged from 0·014% to 2·70%, while chloride content (as NaCl) varied from $<$ 0·02% to 2·69%. However (with the exception of one doubtful sample) larvae were not found breeding in water with a salt content exceeding 0·54% (total) or 0·47% (chloride) and in fact appeared to show a strong preference for fresher water of low salt content. In the doubtful case larvae were found in a stream running into one of the oxidation ponds from an insecticide treated area. The total salt content in the pond was 0·86% and it was not determined whether larvae were living in the mud where sampled or whether they had been washed down following insecticide treatment. The latter appeared more probable. No midges were found in six large areas where the salt concentration exceeded 0·90% NaCl or in four sites where the salt concentration lay between 0·20%–0·35% NaCl.

These results indicate a low salt tolerance in this midge species and suggest a possible means of inhibiting breeding by raising the salt content of the medium. However, the possibility of acclimatisation of the insect to higher salinities cannot be dismissed.

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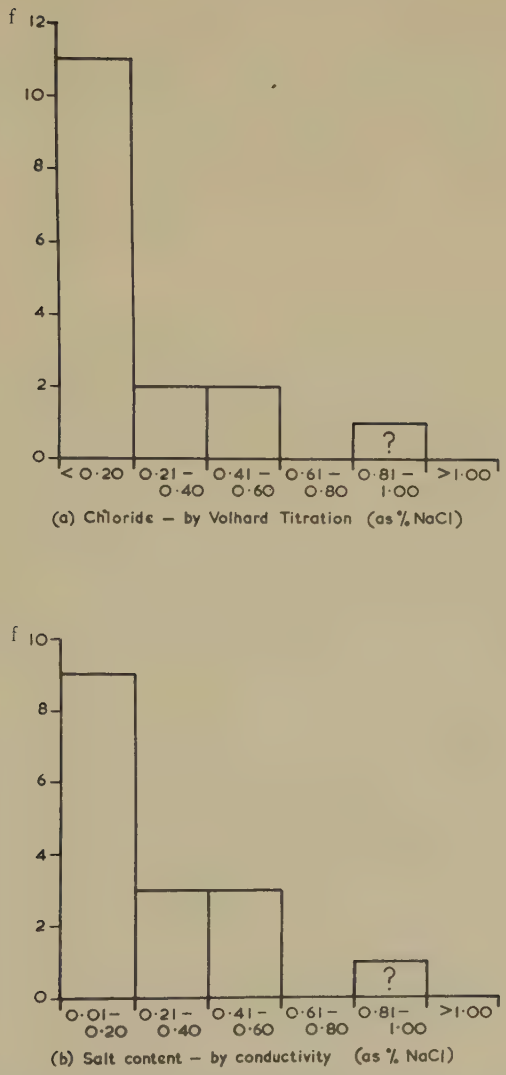

FIG. 1—Distribution of water salinities where larval midges were found. Salt content of water (a) measured as chloride by Volhard titration. (b) Measured by conductivity.

It would appear that the reclaimed areas were particularly favourable for midge breeding when the salt content was lowered by sufficient dilution with fresh water. No correlation was found between pH of the water and frequency of occurrence of midge larvae.

A LABORATORY STUDY OF THE DIFFUSION OF OXYGEN THROUGH PASTURE TOPSOILS

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Summary

Rates of diffusion of atmospheric oxygen through samples of soil into a receiving vessel full of nitrogen gas have been determined by repeated analyses of the gas in the receiving vessel using a Beckman oxygen analyser. The system was tested by placing a perforated plastic disc in place of the soil sample. Rates of diffusion through the disc were in good agreement with those predicted from the total volume of the perforations.

The relationship between intrinsic diffusivity and the percentage of air-space in the soil sample was determined for artificially packed kaolin clay. The clay was made up into two types of sample (1) as crumbs up to 2·0 mm in diameter and containing 24%–28% of moisture on a dry-weight basis; (2) as crumbs less than 0·7 mm in diameter and containing 18%–22% of moisture. Both types of crumb were compacted in thin layers by identical procedures. It was found that the two kinds of crumb yielded different curves when their intrinsic diffusivities were plotted against air-space. No signs of anisotropic diffusion caused by compaction were detected. It was concluded that determinations of the rate of diffusion through artificially packed soil do not represent the behaviour of soil in the field, unless the crumb structure of the latter is closely simulated in the packing.

The relationship between intrinsic diffusivity and air-space was also determined for undisturbed cores cut from the 0·3–1·2 in. depth of three alluvial soils under pasture. Points for all three soils fell on a single curve. It appeared that experimental errors, due to consumption of oxygen in the samples or to the creation of limiting surface layers when the cores were being cut, did not exceed 10% over most of the range of air-space found in the field. The intrinsic diffusivities of the soil were about one-third of those found for perforated plastic discs containing the same percentage of air-pores. It seems that the air-channels in these soils are largely tortuous, blind-ended, or constricted.

The procedure used for measuring intrinsic diffusivities in these tests may be of use as a means of comparing the levels of soil aeration prevailing in different grazing treatments.

INTRODUCTION

Topsoils grazed heavily in winter may contain very low volumes of air pores, accompanied by visible signs of chemical reduction, in the form of a blue colouration characteristic of the gleying process in soils (Gradwell 1956). Such preliminary evidence of poor root aeration indicates the need for an understanding of the processes by which pasture soils obtain oxygen from the atmosphere and for means of measuring the levels of aeration in particular soils. The commonest measure of aeration employed by soil physicists is the percentage of air-filled pores in the total volume of the soil. It is accepted (Russell 1952) that oxygen enters the soil mainly by gaseous diffusion through these pores, displacing carbon dioxide which diffuses in the

opposite direction. The diffusion is blocked equally by soil solids and by water and thus the obstruction to it fluctuates with the moisture content of the soil. Measurements of the rate of diffusion describe only the instantaneous condition of the soil.

The readiness with which a gas diffuses through a material is specified by its coefficient of diffusion, D, which is defined by the relation

$$Q = \frac{DA}{L} (C_1 - C_2) \quad t \qquad \ldots\ldots (1)$$

Here Q is the quantity of gas transmitted in time t; L is the length of the material in the direction of diffusion; A its area of cross-section at right angles to this direction; C_1 is the quantity of the gas in unit volume of space on one side of the material and C_2 that on the other side. Q, C_1 and C_2 are measured in the same units. The diffusion of the gas through the material will be matched by an equal diffusion of another gas moving in the opposite direction (counter-diffusion current). To characterise the properties of the material in a way independent of the particular gas involved, the intrinsic diffusivity, D/D_0 is used. Here D_0 is the coefficient of diffusion of one of the gases into the other in free space at a temperature and pressure equal to those prevailing when D was determined for the soil. In the present work D_0 is obtained from tables. The resistance offered by a given body of the material to gaseous diffusion is represented by its diffusion impedance Z, which equals L/DA.

Thus $$Q/t = \frac{C_1 - C_2}{Z}.$$

For two bodies in series $Z = Z_1 + Z_2$.

The relationship between the volume of air-space in a soil and its intrinsic diffusivity gives an idea of the geometrical form of the air pores; how consistent the relationship is over a group of soils is a measure of how well the coefficient of diffusion can be predicted from the more commonly determined volume of air-space. The relationship has been determined by several observers over the last twenty years. Most of them worked with artificially packed soil, wet or dry, or with other granular materials resembling soil; a few made determinations on cropland soils in the field. All workers found an increasing intrinsic diffusivity as the volume of airspace increased, but their results differ considerably regarding the form of the curve and as to whether it passes through the origin or whether the intrinsic diffusivity falls to zero despite the presence of appreciable airspace. Penman (1940a) measured the rate of diffusion of carbon disulphide through wet and dry soils, artificially packed, and through other materials such as glass spheres. He found a relationship of the form $D/D_0 = 0{\cdot}66S$, where S is air-space volume expressed as a fraction of the whole soil volume. Although his test points did not extend to lower airspace than 0·15, with only one point for soils below $S = 0{\cdot}35$, it appeared that they could be extrapolated back through the origin. Diffusion rates for artificially packed flakes of mica were lower, however, than for other materials of similar airspace, presumably owing to

orientation of the flakes at right angles to the direction of flow. Later Penman (1940b) obtained the same relation, $D/D_0 = 0{\cdot}66S$, for the diffusion of carbon dioxide through dry mixtures of sand, kaolin, and kieselguhr. Van Bavel (1952) studied the diffusion of ethyl alcohol vapour through mixtures of sand, glass beads, and air-dry soil. His results supported Penman's in general but he found D/D_0 about equal to $0{\cdot}6S$. Flegg (1953) took dry soil crumbs in two size ranges, 6 mm to 19 mm in diameter, and less than 6 mm in diameter, packed them on a sieve and wetted them. The rate of diffusion of ether vapour through the soil was tested at various times as it dried. For values of S down to 0·2 he found D/D_0 about equal to $0{\cdot}6S$. Rust, Klute, and Giesecking (1957) measured the diffusion of $^{14}CO_2$ into CO_2 through dry and wet sand, glass beads, and silica flour. They also found D/D_0 proportional to $0{\cdot}6S$, the curve passing approximately through the origin when extrapolated.

Taylor (1949) found, in keeping with Penman, D/D_0 about equal to $0{\cdot}66S$ for the diffusion of oxygen through artificially packed soil. Mixtures of powdered glass and quartz sand, however, yielded different curves which, when extrapolated, reached zero diffusion for S only slightly less than 0·10. This latter type of result was also obtained by Hagan (1941), working with carbon disulphide vapour and artificially packed wet soils. He found that the diffusion rate fell to zero for S values of 0·26–0·29. The relationship was somewhat different for different soils. Blake and Page (1948) carried out measurements in the field on crop soils. D/D_0 for carbon disulphide diffusing upwards from a depth of one foot in wells was related to airspace in the overlying soil. In spite of considerable scatter of points it appeared that, for one soil type at least, diffusion fell to zero at an appreciable airspace.

Considerable effort has been expended by some workers in recognising and correcting for certain sources of error, inherent in the physics of diffusion, which affect the test procedures used in these experiments. These include

(1) The effect of large concentration gradients, needed to produce rates of flow large enough to be readily measurable (diffusion theory applies strictly only to small gradients);

(2) Differences in diffusivity between the diffusing and counter-diffusing gas;

(3) The fact that, when the source of a diffusing vapour is a liquid in a closed vessel underneath the soil sample, the air that forms the counter-diffusion current cannot accumulate in the vessel but returns as part of a mass flow of air and vapour through the soil.

In general, investigations into these difficulties have shown them to introduce errors of only a few per cent into the coefficient of diffusion. Workers adopting methods which eliminated or reduced the errors obtained much the same relationships between intrinsic diffusivity and airspace as earlier workers who did not take such precautions.

It appears to the writer that the differences between the forms of this relationship obtained by different workers are too great to be explained on a basis of errors of diffusion technique: differences in the structure or packing of the soils used in their experiments are more likely to be responsible. Few

workers in this field have described the methods by which they prepared and packed their soils. The results of Blake and Page (1948) for two soils in the field suggest that the form of the curve of D/D_0 against S may differ from soil to soil. However, their results, based on field tests, show such a wide scatter as to obscure somewhat the difference between the two soils.

If the coefficient of diffusion of oxygen through a soil depends on both the amount of airspace and its configuration, then a separate determination of the curve of D/D_0 against S would have to be made for each group of soils thought to have a distinctive form of air channels. As no one has worked on undisturbed pasture topsoils, the determination of the curve for some of these soils was undertaken as part of the present work, together with its re-determination for soil prepared and artificially packed in a controlled manner.

METHODS

Apparatus and Procedure for Diffusion Tests

The diffusion of oxygen into nitrogen was used. These gases have similar diffusivities and are not appreciably soluble in the soil water. The method of Taylor (1949) was followed, the head of partial pressure of oxygen across the soil sample falling during the test. The apparatus was made of aluminium and is illustrated in Fig. 1. The gas chamber *a* had a volume of

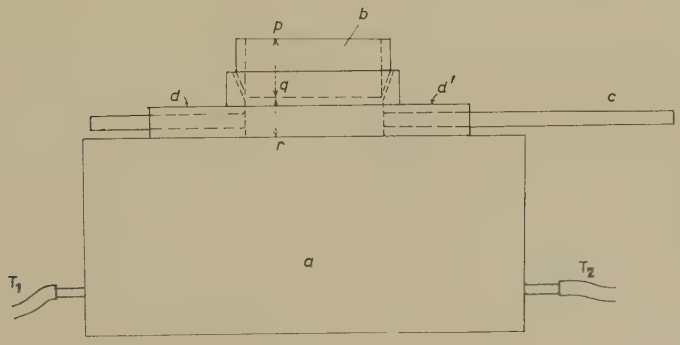

FIG. 1—Diagram of Gas Vessel and Sample Holder.

approximately 2·5 litres and the soil sample *b*, enclosed in a brass cylinder 7·6 cm in diameter with a cutting edge, fitted closely into a hole in its top and was sealed around with petroleum jelly. Just below the lower surface of the soil sample ran the sliding plate *c*, closely fitted into guides on every side and lubricated with petroleum jelly to provide a gas-tight seal. When *c* was pushed to the left it isolated *b* from *a*. When it was pushed to the right a circular opening 7·6 cm in diameter came opposite the base of *b* and permitted gases to flow from the atmosphere through *b* and into *a*. At the start of a test, cylinder nitrogen was flushed through *a* by means of the tubes T_1 T_2 until the oxygen content of *a* was near zero. The supply of nitrogen

was then cut off and one of the tubes T_1 T_2 opened to the atmosphere for a few minutes to permit the gas in *a* to come to atmospheric pressure. Then the trap *c* was opened and atmospheric oxygen allowed to diffuse through the soil into *a*. At intervals *c* was shut and the gas in *a* mixed and circulated through a Beckman D2 oxygen analyser by means of a rubber suction bulb in a closed circuit of tubing running from T_1 to T_2. The oxygen content of the gas was then read and *c* reopened so that the flow of gas into *a* resumed. By a series of such readings the quantity of oxygen diffusing into *a* could be computed from the known volume of *a*. The first reading was discarded as this was rendered unreliable by the air initially trapped under the soil sample in fitting it into its socket above the sliding trap. A few dummy runs were made without opening the slide and it was found that the rate of leakage of oxygen into the gas vessel was too low to have any significant effect on the test results.

In this apparatus we have the quantity δQ of oxygen entering *a* in the short time δt. Now $\delta Q = V.\ \delta C$ where V is the volume of tank *a* and C the oxygen content of the gas in it expressed as a fraction of the whole. If C_0 is the oxygen content of the atmosphere we have

$$V.\ \delta C = \frac{DA}{L}\ (C_0 - C)\ \delta t \quad \text{from (1)}$$

$$\frac{\delta C}{C_0 - C} = \frac{DA}{VL}\ \delta t$$

hence $\log_{10} \dfrac{C_0}{C_0 - C} = \dfrac{DAt}{2{\cdot}303VL}$ integrating from C = O to C.

The values of $\dfrac{C_0}{C_0 - C}$ for successive readings of C were plotted logarithmically against t. The time interval, Δt, which elapsed as $\dfrac{C_0}{C_0 - C}$ increased from 1 to 10 was read from the graph. Over this interval $\log_{10} \dfrac{C_0}{C_0 - C}$ increased by unity. Hence $\dfrac{1}{\Delta t} = \dfrac{DA}{2{\cdot}303VL,}$ and D was computed from this relationship.

Referring now to Fig. 1 it can be seen that when the sliding trap *c* is in the open position, gas diffusing into tank *a* must, after traversing the thickness *pq* of the soil sample, also flow for the distance *qr* through a narrow neck in the apparatus before entering the body of the gas vessel. The diffusion impedance of this neck, Z_1, is in series with that of the soil core, Z, and it is

the total impedance, $Z + Z_1$, which determines the rate of gaseous diffusion into the apparatus and hence the coefficient of diffusion as calculated above. The drop in partial pressure of oxygen across the sample during flow will be $\frac{Z}{Z + Z_1}$ of the drop between the atmosphere and the gas in *a*. Hence the apparent coefficient of diffusion as calculated above must be multiplied by a correction factor $1 + \frac{Z_1}{Z}$ to obtain the true D value for the soil.

$$D = D_{app}\left(1 + \frac{Z_1}{Z}\right) = D_{app}\left(1 + \frac{L_1}{D_0 A_1} \cdot \frac{DA}{L}\right)$$

L and A are the dimensions of the soil core, L_1 and A_1 of the neck and D_0 is the coefficient of diffusion of oxygen into nitrogen in free space, which is known. Hence D may be calculated from D_{app}. It is this corrected value of D which was used in calculating all values of intrinsic diffusivity D/D_0 quoted in the results. The effect of the correction ranged from an increase of 10% in the value of D for the driest soil samples tested to an increase of less than 1% for the wettest samples.

Experimental Calibrations of Oxygen Analyser and of Diffusion System

The Beckman oxygen analyser, used here for quick determinations of the oxygen content of gas mixtures, gives a scale deflection proportional to the intensity of magnetisation induced in the gas by the field of a permanent magnet (Pauling, Wood, and Sturdivant 1946). Of the gases normally encountered in the atmosphere only oxygen has an appreciable magnetic susceptibility. The susceptibility is influenced by temperature throughout the scale (from 0 to 25% oxygen) and by barometric pressure throughout except at the zero oxygen end. The influence of atmospheric pressure is exerted through its effect on the number of oxygen molecules in unit volume. An approximate correction of the readings of the analyser for these factors was made as follows. The gas vessel *a* was filled with nearly pure, commercially obtained nitrogen and readings were made on the analyser at a number of temperatures covering the range normally encountered. From these a curve of instrument readings for zero oxygen was drawn against temperature. Before each experimental run a reading was taken on atmospheric air; this gave the instrument reading for 20·9% of oxygen at the temperature and pressure prevailing. A graph was drawn with instrument reading as abscissa and true oxygen content as ordinate. The point determined for atmospheric air was plotted and joined by a straight line to the point for zero oxygen at the temperature prevailing. Readings taken in the test run were corrected immediately by means of this line.

Some corrected readings on gas mixtures were compared with oxygen contents determined by absorption in a solution of pyrogallic acid in strong potassium hydroxide. Commercially obtained nitrogen was mixed with air

in the gas vessel and a reading taken on the Beckman analyser. A sample was then drawn off into the gas pipette of a Haldane apparatus (Haldane and Graham 1935) for absorption in pyrogallate. The Haldane apparatus was itself standardised on outside air. After a suitable correction was made for the fact that the Beckman apparatus analyses dry air and the Haldane apparatus air saturated with water vapour, the readings of the two instruments compared as in Table 1.

TABLE 1—Comparison of Oxygen Contents of Gases Analysed by Two Methods

By Beckman Analyser (Corrected for Temperature and Pressure)	*By Haldane Apparatus* (Per Cent Oxygen in Dry Gas)
20.9	20.81
15.4	15.33
11.3	11.49
8.2	8.46
6.4	6.63
4.5	4.75
2.2	2.31
0.2	0.28

The differences between the two methods are slight. It was found that the substitution of figures from the Haldane apparatus for those from the Beckman analyser raised the coefficients of diffusion experimentally obtained by 3% of their value, on the average. A calibration curve was drawn from the figures in Table 1 and was used to make a further correction of the oxygen contents given by the Beckman apparatus.

The diffusion system as a whole was checked by carrying out test runs with the soil sample replaced by a disc of a solid plastic material sealed into place and perforated by a number of drillholes, 2 mm in diameter, normal to the surface. Between runs additional holes were drilled, their aggregate volume being found from the loss in volume of the disc as determined by displacement of water. The rate of gaseous diffusion through straight pores of uniform diameter normal to the surface of a body is proportional to the aggregate cross-sectional area of the pores. The intrinsic diffusivity (D/D_0) for such a body should, theoretically, equal its airspace. Airspace is reckoned as volume of pores divided by total volume of the disc, including pores. The results of the diffusion runs through perforated discs are plotted in Fig. 2. It can be seen that experimental values of D/D_0 are close to the theoretical values. These tests showed no evidence of systematic error in values of D/D_0 determined by the apparatus. The value of D_0 computed from these tests did not differ by more than the experimental error from the value derived from tables.

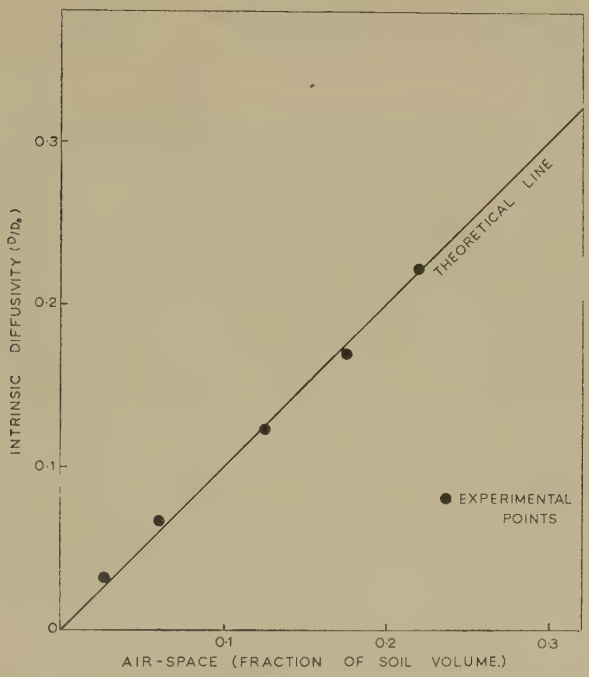

FIG. 2—Relation between Intrinsic Diffusivity and Air-space for Perforated Plastic Disc.

Tests on Artificially Packed Soil

The soil chosen for this work was a kaolin clay containing no organic matter. This was oven-dried at 105°C and ground. It was then wetted to the required moisture content by spraying and mixing with a spatula. The crumbs so formed were broken by hand to pass through a sieve and were left loosely packed in a jar for an hour to allow their moisture content to become more uniform throughout. Two different modes of preparation were adopted, (a) wetting to a moisture content between 24% and 28% on a dry weight basis and passing through a sieve of 2·0 mm aperture, or, (b) wetting to a moisture content between 18% and 22% and passing through a sieve of 0·7 mm aperture. After standing for an hour the crumbs were packed in layers into the cutting cylinder in which they were to be held for the diffusion test. Each layer was compacted before the next was added, sufficient crumbs being added at each stage to form a layer about 4 mm thick after compaction. The desired airspace was obtained by controlling the intensity of compaction. The lighter compactions were produced by repeatedly applying finger pressure over the surface of the layer of crumbs to give as uniform a coverage as possible. The heaviest compactions were obtained by tamping the kaolin with the end of a brass cylinder $1\frac{1}{2}$ in. in diameter. Most of the cylinders of compacted soil prepared were 3·0 in. in diameter and 0·9 in.

long but some cylinders 3·0 in. long were prepared. To prevent the less compact samples from falling out of the bottom of the cylinders the soil was seated on a gauze glued to the end of the cylinder. The gauze was composed of wire 0·25 mm in diameter and had openings 1·0 mm square. A test on one of the more heavily compacted samples without a gauze yielded a coefficient of diffusion in close agreement with those from similar samples with gauzes. It was concluded that the gauze impedance was slight, as would be expected from theoretical considerations, and it was disregarded. During packing, the bottom layer of crumbs rested on a hard surface and so could have been more severely compacted than the rest of the core. After the test on one core the bottom quarter of an inch was removed and the test repeated. The coefficient of diffusion was greater by only 5% to 10%, which suggests that this effect is not a serious one. Some tests were made to determine whether the coefficient of diffusion through the samples in the direction of compaction differed from the coefficient in a direction at right angles to that of compaction. Kaolin clay was prepared and rather heavily compacted, by the procedures described above, into a cubic box with sides 5 cm long, and open at the top and bottom. A diffusion run was made on the sample. Afterwards, its top and bottom were sealed with molten petroleum jelly and two opposite sides of the box removed. A second diffusion run was then made with the gas flowing between these two sides.

Tests on Undisturbed Pasture Topsoils

The visible signs of remoulding and of chemical reduction in wet pasture soils are concentrated in the surface inch or two. It seems likely that the obstruction to the diffusion of oxygen into the soil is mainly in this layer. Hence all tests were made on samples taken from it. Undisturbed cores were cut by hand from the 0–1½ in. depth and brought to the laboratory, where the final cutting of the test sample could be done with more care. The central portion of the samples, representing the 0·3 in. to 1·2 in. depth of the soil in the field, was cut to fit into a test cylinder 3 in. in diameter. The cutting procedure has been more fully described elsewhere (Gradwell 1960).

Any gaps between the soil and the cylinder were filled with remoulded soil. A few tests were made with the gaps left unfilled. The coefficients of diffusion so derived did not differ significantly from those for soil cores of equal airspace with the gaps filled. Nevertheless, the plugging of these gaps was continued in order to guard against any leakage of gas down the side of the soil samples.

The ends of the core were then cut to flat surfaces with a razor blade. The surfaces were approximately co-planar with the ends of the test cylinder but the cutting of a surface as free as possible from smearing and puddling was given priority over the accurate shaping of the surface. Naturally, no attempt was made to refill any small depressions in the end surfaces of the cores which were accidentally produced during cutting and at the points where such depressions were present the cores were somewhat shorter than

their nominal length. It is considered, however, that the mean length of a test core would be within a few per cent of the length of the cylinder containing it.

When a diffusion test was finished the core was removed from the gas vessel and its ends carefully cut to a plane surface, as determined by a straight edge. Any depressions below this surface were now plugged with remoulded material. The core was then removed from the test cylinder and any depressions in its cylindrical face also plugged with remoulded material. The airspace in the core was now determined by weighing it and drying it in an oven at 105°C (Gradwell 1960) using known values for the specific gravity of the soil. It was found that the samples lost about 1 g of water through evaporation during a diffusion test. Accordingly, each core was weighed before and after and the difference added to the final wet weight of the core to compute its volume of airspace. Thus the airspaces quoted represent the condition of the cores at the beginning of the test: at the close of the test the volumes of airspace may have been about 0·01 higher for each core.

Consumption of Oxygen by Undisturbed Pasture Topsoils

It was realised that coefficients of diffusion derived from the rate at which oxygen arrived in the gas vessel after passing through the test cores would be erroneously low if any appreciable amount of oxygen was consumed in the soil. Accordingly, side experiments were set up to determine the oxygen consumption of the cores under conditions similar to those of the main experiments. A soil core was fitted into the top of the gas vessel in the normal way and another vessel, of about 3 litres capacity, was placed over the sample so as to enclose it, and sealed down to the top of the gas vessel by means of screws and a rubber sealing ring. The sealing ring bore down on points dd′ in Fig. 1. The upper vessel was fitted with tubes by which it could be connected to the oxygen analyser circuit. At the start of a test the lower gas vessel and the space under the sample were filled with nitrogen and the upper vessel with air. The slide was then opened for about an hour. At the end of that time it was closed and the oxygen analyser connected first to the lower vessel and then to the upper one for determinations of gas composition. The analysis of the gas in the upper vessel was corrected for the gas carried over in the analyser circuit from the previous analysis on the gas in the lower vessel. After this correction had been made, the consumption of oxygen in the soil core was taken as the difference between oxygen loss from the upper vessel and oxygen gain in the lower vessel. This consumption was recorded as a percentage of the diffusion into the lower vessel.

Probable inaccuracies in estimating the volumes of the gas vessels could create fairly large errors in the consumption of oxygen so derived. As a check on this, blank determinations of consumption were made on artificially-packed, biologically-inert kaolin clay.

Effect of Artificially Cut Soil Surfaces on Diffusion Rate

The relating of D/D_0 and the airspace in a soil sample is meaningful only if there are no thin layers in the core limiting diffusion. In any method of measuring the rate at which oxygen diffuses down in the soil, the creation

of an artificial surface in the soil seems inescapable. It is a matter of concern, therefore, whether the cut surfaces used in the present investigation were limiting gaseous diffusion. If Z were the *in situ* diffusion impedance of the soil core and Z_0 the additional impedance contributed by puddling action on a cut surface, then the measured impedance of the core, with an upper and a lower cut surface, would be $Z + 2 Z_0$. Some attempts were therefore made to measure Z_0.

The effect of the upper cut surface was first investigated. Nine cores were tested with the surface layer of the soil still intact, rising approximately 0·3 in. above the upper rim of the test cylinder. The cylindrical face of the soil was coated with petroleum jelly where it was exposed. Thus all oxygen entering the core did so through the natural soil surface. After a test run was made on a sample thus prepared, its top portion was cut off flush with the upper rim of the test cylinder and a second test made. In order to compute the coefficient of diffusion for the first test a figure was needed for the length of the core before its surface layer was cut off. As natural soil surfaces are irregular this was obtained not by measurement but by weighing the soil cut off after the first run and assuming that the density of the soil was uniform throughout.

The effect of a change in the nature of the lower surface upon the diffusion coefficient of the core was also investigated. Three of the wetter cores were tested with the natural soil surface forming their upper boundary. The lower surfaces of two of them were formed by picking off unwanted soil in small lumps with the point of a penknife. This produced a surface of which at least half the area had been formed by soil breaking in tension. After a test run the lower boundaries were trimmed off with a razor blade to produce an entirely cut surface. A second test run was then made. As in the previous series of experiments, the change in length of the core during the cutting was computed from its loss of weight. The third core was tested first with an ordinary cut lower surface. This was then picked away with the knife point and a second test made. These experiments were carried out on cores with airspaces of approximately 10% and D/D_0 values of 0·015 to 0·02.

A further study of the properties of a cut lower boundary was made by means of a masking technique derived from that of Domby and Kohnke (1956). These tests were also made on cores with the natural soil surface as their upper boundary. Their lower surfaces were cut with a razor blade as for a normal test. After a test run had been made their lower surfaces were partly covered with concentric circular strips of petroleum jelly about 0·3 in. wide, applied through the slots of a pattern cut from a stiff plastic sheet. The bands of unmasked soil between the strips were about 0·25 in. wide. The proportion of the soil surface thus masked was determined by weighing the plastic pattern and also the strips cut from it. The proportion of the latter in the total weight of plastic was taken as the fraction of the soil surface masked by petroleum jelly, being about 0·55 in this series of tests. When the petroleum mask was applied the soil core was replaced on the gas vessel and another test run made. The percentage decline in diffusion rate was noted.

The principle of this method is that, if the mask is applied over a surface already strongly limiting diffusion, the further reduction of flow will be considerable. These experiments were carried out on cores containing about 20% of airspace.

All of the last three series of experiments – the cutting off of the uppermost layer of the soil, the comparison of a cut and a picked surface and the masking of the lower surface – depend upon a comparison between two diffusion runs taken at an interval of about two hours. Over this period a core could dry out sufficiently to increase its diffusion rate in the second test and so confuse the change due to the treatment applied. This factor was investigated by doing an ordinary test run on a core, storing it in the room for some time without any treatment and then doing a second run two hours after the first. Two cores so treated showed increases of 5% and 6% in their rates of diffusion. The results of all three series of experiments detailed above were accordingly corrected for drying error by reducing the result of the second test run on each core by 5·5%.

SOILS

Rates of diffusion of oxygen through undisturbed pasture topsoils were mostly determined at natural moisture content. To obtain tests over a wide range of airspace it was necessary to choose sampling sites which could be visited at short notice when soil moisture was at some desired level. Several visits to each site were also needed. To meet these requirements three sites on local alluvial soils were chosen. All were silt loams.

(1) Manawatu silt loam at Grasslands Division, Palmerston North—a recent soil under a ryegrass - white clover pasture;

(2) Heretaunga mottled silt loam at the Soil Bureau Experimental Station, Taita—a gleyed recent soil under a mixed, rather rooty pasture with many flatweeds;

(3) Gollans silt loam at Wallaceville Animal Research Station, Upper Hutt—a gley soil under a ryegrass-clover pasture.

On each site samplings were spread throughout a year, the samples with the lowest contents of airspace being taken in winter and those with the highest contents in late summer. From two to four cores were taken at each sampling, the replicates being carved from points within a few yards of one another. The cores of Heretaunga mottled silt loam appeared to have a greater volume of free-draining pores than the other two soils. On most of the occasions when this was measured the samples of Heretaunga mottled silt loam contained 15% to 20% of pores drained at a suction of 50 cm of water; the samples from the other two soil types had 5% to 10% of such pores.

In addition to samples tested at field moisture, some samples of Manawatu silt loam and Heretaunga mottled silt loam were saturated and drained at a suction of 50 cm of water. Test cores were then taken from them for the determination of the rate of oxygen diffusion.

RESULTS

The relationship between intrinsic diffusivity and airspace for cylinders of artificially packed kaolin, is plotted in Fig. 3. It is seen that the test results fall into two distinct curves according to the mode of preparation of the soil. Larger and wetter crumbs permit a higher rate of gaseous diffusion for a given volume of airspace. It appears, from an extrapolation of the curves, that the rate of diffusion would be zero in a sample with as much as 0·1 to 0·2 of relative airspace. Results for test cores 3 in. long agreed well with results for cores 0·9 in. long.

The coefficients of diffusion of oxygen through cubic blocks of artificially packed kaolin in the direction of compaction and at right angles to it were not significantly different. There was no indication that the low rates of diffusion through the cylindrical samples (measured in every case in the direction of compaction) were due to anisotropy produced by the compaction. The intrinsic diffusivities derived from the tests on cubic samples are also plotted in Fig. 3. It is seen that the points lie in the same general region as those derived from the cylindrical samples, but they scatter more widely, as determinations of airspace in the cubic samples could not be made accurately.

In Fig. 4 the intrinsic diffusivities for undisturbed cores of pasture topsoils are plotted against their airspace. On the same figure is re-drawn the theoretical line for a core containing only straight pores of uniform cross-section normal to the surface of the core. The relationship between D/D_0 and S appears to be consistent over all the soil samples tested. Cores soaked and drained to 50 cm of suction before the test yielded intrinsic diffusivities similar to those from cores tested at natural moisture content, provided airspaces were the same. Diffusion rates for cores of Manawatu silt loam and Heretaunga mottled silt loam were not noticeably different when these soils had similar airspaces, although their contents of free-draining pores were quite different (see above under "Soils"). In general, intrinsic diffusivities for a given airspace were about one quarter of what could be expected from an equal volume of straight, uniform pores running normally to the surface of the core.

Intrinsic diffusivities for those undisturbed topsoil cores which were tested at their natural moisture are also set out in Table 2. In this table the results from cores taken at a single sampling are grouped together. The coefficient of variation is also tabulated for each sampling. These coefficients range downwards from 41·2% and do not appear to depend upon the mean diffusivity derived from the sampling.

The proportion of diffusing oxygen consumed in passing through topsoil cores is set out in Table 3 (a). The mean consumption is seen to be about 1% for moist cores and 9% for wet cores. In Table 3 (b) are set out the results of similar tests on inert kaolin. These results give an idea of the size of the experimental errors in the determinations of oxygen consumption. As there could be no consumption of oxygen the negative results must represent an experimental error.

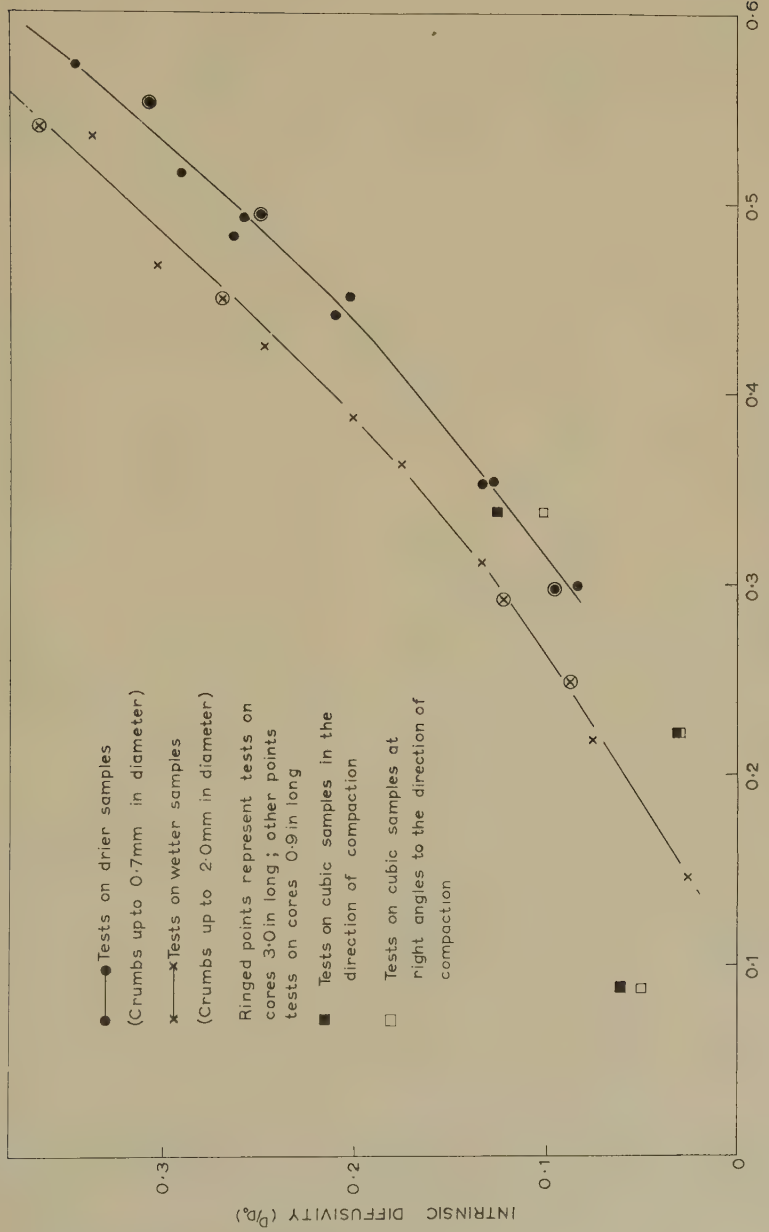

FIG. 3—Relation between Intrinsic Diffusivity and Air-space for Artificially Packed Kaolin Clay.

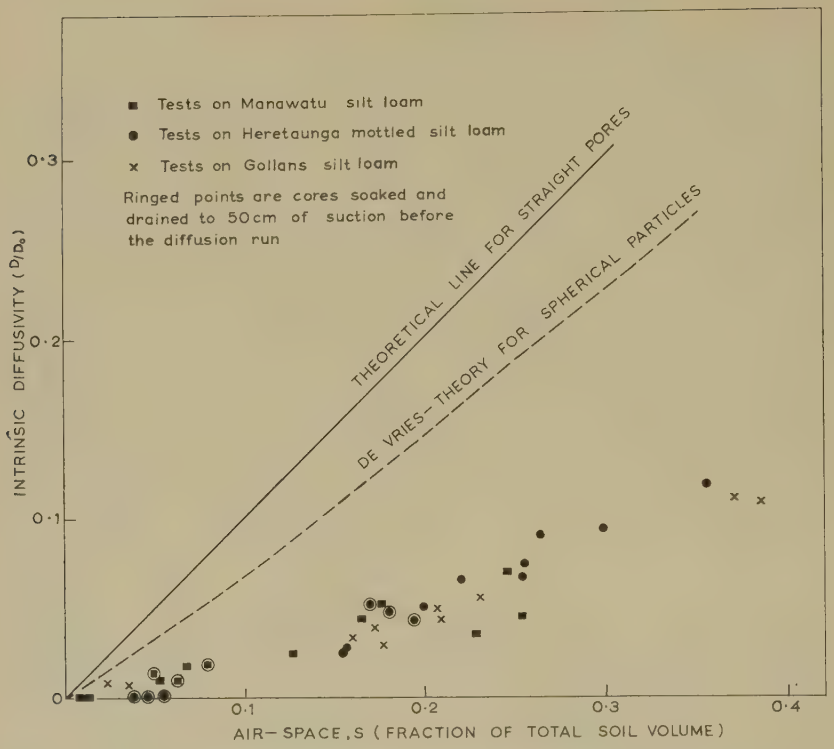

FIG. 4—Relation between Intrinsic Diffusivity and Air-space for Undisturbed Samples of Pasture Topsoils.

The results of experiments in which the uppermost 0·3 in. of the soil was cut off are set out in Table 4. No reduction of diffusion resulting from the creation of an upper cut surface is evident in the figures – on the contrary, the mean coefficient of diffusion for the 0·3 to 1·2 in. depth is about 5% higher than that of the 0 to 1·2 in. depth.

Changing the lower boundaries of two cores from surfaces largely broken in tension to entirely cut surfaces decreased the diffusion coefficients of the cores by 14% and 6% respectively; making the reverse change on a third core raised its coefficient of diffusion by 13%.

The results of the masking experiments are set out in Table 5. Masking 55% of the lower surfaces of cores in strips reduced the coefficient of diffusion by an average amount of 9%, with a maximum reduction of 14%. Working with samples of similar thickness in which the absence of a surface layer limiting to diffusion had been demonstrated. Domby and Kohnke (1956) found that a mask covering 55% of the surface of the soil reduced the rate of gaseous diffusion by about 10%. The fact that the results reported here are in agreement with those of Domby and Kohnke is further evidence that the surface layer was not limiting to diffusion.

TABLE 2—Intrinsic Diffusivities for Undisturbed Cores of Pasture Topsoil Tested at Natural Field Moisture

Soil Type and Sampling Occasion		Sample No.	Intrinsic Diffusivity (D/D_0)	Coefficient of Variation for Sampling Occasion (%)
Heretaunga mottled silt loam	First Sampling	1	0.123	
		2	0.126	2.6
	Second Sampling	1	0.068	
		2	0.074	6.3
	Third Sampling	1	0.068	
		2	0.093	22.0
	Fourth Sampling	1	0.088	
		2	0.065	21.6
	Fifth Sampling	1	0.024	
		2	0.027	8.9
Manawatu silt loam	First Sampling	1	0.011	
		2	0.016	27.7
	Second Sampling	1	0.070	
		2	0.023	
		3	0.050	
		4	0.044	41.2
	Third Sampling	1	0.043	
		2	0.038	9.0
Gollans silt loam	First Sampling	1	0.108	
		2	0.119	6.8
	Second Sampling	1	0.048	
		2	0.042	
		3	0.060	18.3
	Third Sampling	1	0.024	
		2	0.028	10.9
	Fourth Sampling	1	0.027	
		2	0.044	
		3	0.033	
		4	0.054	30.0
	Fifth Sampling	1	0.0087	
		2	0.0078	7.7

TABLE 3 (a)—Consumption of Oxygen by Cores of Pasture Topsoil During Diffusion Runs

Sample	Oxygen Entering Core (ml at room temperature and pressure)	Oxygen Emerging from Core	Apparent Gain (%)
Moist cores			
Heretaunga 1	123.0	121.1	−1.6
Heretaunga 2	110.2	113.5	+3.0
Heretaunga 3	133.2	128.1	−3.8
Heretaunga 4	134.2	134.6	+0.3
Gollans 1	123.4	119.3	−3.3
Mean of Moist cores			−1.1
Wet cores			
Manawatu 1	68.2	61.5	−9.7
Gollans 2	49.6	45.0	−9.2
Mean of Wet cores			−9.4

TABLE 3 (b)—Apparent Consumption of Oxygen by Artificially Packed Kaolin

Sample	Oxygen Entering Sample (ml at room temperature and pressure)	Oxygen Emerging from Core	Apparent Gain (%)
Loosely packed samples 1	183.1	187.6	+2.5
2	114.7	114.8	+0.1
3	124.0	125.4	+1.2
4	127.1	133.3	+4.9
5	89.9	93.7	+4.2
6	60.5	62.0	+2.5
Mean of Loose Samples			+2.6
Moist, tightly packed samples 1	49.6	55.0	+10.8
2	53.4	57.9	+8.5
3	37.2	39.4	+5.9
Mean of Tight Samples			+8.4%

TABLE 4—Effect of Cutting Off the Surface Layer on the Coefficient of Diffusion of Oxygen Through Topsoil Cores

Description of Samples	Coefficients of Diffusion of Cores with the Natural Soil Surface as Their Upper Boundary (cm^2/sec)	Coefficients of Diffusion After the Cutting of an Artificial Upper Surface (cm^2/sec)	Gain or Loss (%)
Heretaunga, dry core	0.0243	0.0230	−5
Heretaunga, dry core	0.0229	0.0237	+4
Heretaunga, moist core	0.0135	0.0139	+3
Heretaunga, wet core	0.0085	0.0087	+2
Heretaunga, wet core	0.0040	0.0045	+12
Gollans, moist core	0.0087	0.0093	+7
Gollans, wet core	0.0013	0.0014	+8
Manawatu, moist core	0.0083	0.0093	+12
Manawatu, wet core	0.0020	0.0020	0
Mean gain			+5

TABLE 5—Effect of Masking Strips of the Cut Surface of a Core With a Material Impervious to Gaseous Oxygen

	Original Coefficient of Diffusion of Core (cm^2 sec^{-1})	Proportion of Area of Lower Core Surface Covered by Mask (%)	Reduction in Coefficient of Diffusion (%)
Test 1	0.015	60	11.6
Test 2	0.0023	57	3.0
Test 3	0.020	55	13.9
Test 4	0.015	56	6.2
Test 5	0.011	56	11.1

DISCUSSION

The results of the tests on artificially packed kaolin support those workers who have found that soil, or other granular materials, can be packed so that the rate of gaseous diffusion through them approaches zero at appreciable airspace. In the present work the low rates of diffusion do not seem attributable to crumb flattening or to alternating dense and loose layers produced by compaction; these effects would probably give rise to a lower rate of diffusion in the direction of compaction than at right angles to it, which was not observed. The different relationships between intrinsic diffusivity and airspace found for cores compacted from soil crumbs of different sizes and moisture contents illustrate the difficulty of predicting the behaviour of soils in the field from observations of soil packed in a single arbitrarily chosen manner in the laboratory, much less from granular materials other than soil. The comparison of curves of D/D_0 against airspace, for soils of two different aggregate sizes, has been attempted previously only by Flegg (1953), who found little difference. All his crumbs were, however, considerably larger than those used in the present work and, furthermore, it is not clear whether the difference in crumb size was accompanied by a difference in moisture content, as it was here. Lower intrinsic diffusivities, at given airspace, for the smaller and drier crumbs may have been caused by a greater tendency for small crumbs to form enclosed spaces when compacted or by the concentration of a higher proportion of their airspace inside the crumbs, leaving less in passages running between them. In any case it is clear that a considerable proportion of the air-pores in the artificially packed kaolin was in forms contributing little to diffusion – tortuous, blind-end, or totally enclosed pores, or channels whose alternate narrowings and widenings gave them a diffusion impedance out of proportion to their total volume. It also seems that the incidence of such forms can depend upon the structure of a soil. The consistency of the relationship between diffusion rate and airspace for undisturbed samples of pasture topsoil indicates that the structure factor is a constant for them, at least over the three soils studied. The fact that the curves of intrinsic diffusivity plotted against airspace for artificially packed kaolin extrapolate to zero diffusion for airspace volumes of 10% to 20% seems to indicate that about this proportion of totally enclosed air pores was present in this material.

The main objection to using the gaseous diffusion rate as a measure of the aeration status of the soil, as it affects plant roots, is that the diffusion through an appreciable volume of soil is integrated by the measuring device. Thus a disproportionate amount of the measured diffusion may take place through the larger, air-filled, fissures in the soil, while the centres of the aggregates are nearly saturated and receive little aeration. This would apply particularly to loose granular soils. The appearance of heavily grazed pasture topsoils encourages the belief that measured rates of gaseous diffusion through them may be representative of the whole soil. Aggregates are usually obliterated, particularly in winter, when the measurement of aeration is most required, and the soil becomes a nearly uniform mass in which the only large drained channels evident are the wormholes. Up to four wormholes, each about 4 mm in diameter have been found in test cores 7·6 cm in

diameter. These contribute about 1% of air-space in a soil which may contain about 5% or 10% of airspace altogether. Treating the wormholes as straight pores of uniform section normal to the surface of the core (as they very nearly are) it can be calculated that they will raise the intrinsic diffusivity by 0·01. In the region of lowest airspace (less than 5% of the soil volume) this is about equal to the highest intrinsic diffusivities found, and it seems that wormholes may be mainly responsible for the flow measured. In the high and medium range of airspace the contribution of wormholes to diffusion is proportionately small, and it does not seem likely from the plotted results that the diffusion of oxygen through the soil mass other than through the wormholes can be negligible for air spaces above 5%.

In gaseous diffusion the contribution of the larger channels is not as great as in water percolation, since diffusion through a tube is proportional to the square of the radius and water flow to the fourth power of the radius. The fact that the occasional large crack or wormhole contributes much less to the rate of oxygen diffusion than to water permeability is reflected in the low coefficients of variation of the former measurement, averaging 16% over several groups of replicates. By contrast, determinations of the rate of water infiltration into cores of similar diameter similarly spaced in pastures have yielded a mean coefficient of variation of nearly 100% (Gradwell 1958). Because of the high variances found it has been considered that the information gained from soil core studies of the percolation rate of water is of questionable value (Toogood 1956). It seems that from this point of view the rate of oxygen diffusion through cores offers better promise of detecting differences between treatments. To ensure that the measured differences represent rates of diffusion through the whole soil mass it would be necessary to check that the theoretical contribution of the wormholes to diffusion was a small fraction of the diffusions measured.

The coefficient of oxygen diffusion does not describe completely the aeration conditions in a soil. The theory of van Bavel (1951) illustrates how the concentration of oxygen in the air-pores of a soil in the field depends upon the rate of production of carbon dioxide as well as upon the coefficient of gaseous diffusion. Raney (1949) has recorded a case where a treatment which greatly increased the production of carbon dioxide (addition of organic matter) resulted in lower partial pressures of oxygen than were found in the control, although the intrinsic diffusivity was higher in the treated soil. Direct measurements of the contents of oxygen or carbon dioxide in soil air have a limited value for predicting the responses of plants to different conditions of aeration. This is because the gas analysed is withdrawn, by existing sampling techniques, from the large voids in the soil, which quite likely have a higher concentration of oxygen than occurs at the root-soil interface (Russell 1952). In trials where the rate of evolution of carbon dioxide in the field is not likely to differ between treatments, or has been shown not to, measured rates of oxygen diffusion probably permit the arrangement of treatments in their correct order in terms of the composition of the soil air at a given depth.

Turning now from the value of the method for detecting aeration differences to its absolute accuracy, the question arises: does the relation between intrinsic diffusivity and airspace plotted for cores in the laboratory

apply to soil in its natural profile in the field? Measurements of oxygen consumption under laboratory conditions show that values of D/D_0 are underestimated, owing to consumption, by a few per cent over most of the range of airspace but by almost 10% at the lowest airspaces. Experiments to investigate the influence of the artificially cut surfaces on the cores indicated that the cutting of the lower surface may reduce diffusion by 10%. On the other hand, the removal of the top 0·3 in. of the soil raised the diffusion by about 5%. According to such methods as are available for testing the effect of cut surfaces, it would appear, therefore, that the measured coefficient of diffusion for the 0·3 to 1.2 in. depth of the soil is not greatly different from the actual coefficient of diffusion of the 0 to 1·2 in. depth in the field. Some other small sources of error, largely mutually compensating, are present in the tests. Depressions in the plane surfaces of the cores, formed in cutting, reduce their mean length below the nominal value used in computing D. This makes the results a few per cent high. On the other hand, the plugging of similar cavities in the cylindrical surfaces with remoulded material impenetrable to gases, reduces the effective cross section of the cores. This may reduce D by a few per cent. Other small errors may remain in the apparatus or diffusion procedure or arise from soil drying during the test, despite the corrections applied for these factors. Taking all these errors into account, it does not seem probable that the values of intrinsic diffusivity plotted in Fig. 4 are low by more than 5% to 10% over most of the range of airspace or by 20% to 25% at the lowest values of airspace. These errors are smaller than the variations between cores.

The experimentally determined values fall well below the theoretical line for straight pores of uniform cross-section running at right angles to the core face. It thus seems that tortuous, blind-ended, or locally constricted air-pores must be a prominent feature of the pasture topsoils studied. De Vries (1950) has derived theoretically the intrinsic diffusivity through a medium of spherical particles, in terms of its airspace. His curve is plotted in Fig. 4 (broken line). He has taken account of possible reduction of diffusion rates, below the levels indicated by the curve, caused by the presence of a proportion of blocked pores. The volume fraction occupied by blocked pores is taken as $\beta(1 - S)$, where β is a constant for the soil and S is airspace as before. This means that the proportion of blocked pores increases from 0 at $S = 1$ to β at $S = 0$. Fairly good agreement with the experimental points of the present investigation was obtained by multiplying the theoretical diffusion rate between $S = 0{\cdot}1$ and $S = 0{\cdot}4$ by a constant factor of 0·3. This would seem to indicate that the proportion of blocked pores does not change much over this range of airspace. For airspaces below 0·1 the influence of wormholes and the scatter between determinations become proportionately too great to permit of precise conclusions.

CONCLUSIONS

Determinations of rates of gaseous diffusion through artificially constituted soil are likely to have little application in the field unless the manner of preparation and packing closely simulate the structure of soil in the field.

Rates of diffusion through three alluvial soils indicate the presence of a high and rather constant proportion of blocked or tortuous air-pores, which are ineffective as channels of aeration.

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THE TRANSFORMATION OF COUNTS OF THE CABBAGE APHID (*Brevicoryne Brassicae* (L.))

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Summary

Counts of cabbage aphids are unsuitable for direct statistical analysis because their error variance increases with their mean according to the relation

$$v = 3{\cdot}42m^{1{\cdot}65}$$

This suggests that the count c be transformed to the fractional power $c^{0{\cdot}175}$ to stabilise the variance. This transformation does indeed stabilise the variance but at a higher value than expected. The inverse hyperbolic sine and the $\log(c + 1)$ transformations are nearly as effective as the fractional power and, on the grounds of availability of tables, $\log(c + 1)$ is recommended as the best transformation for counts of cabbage aphids in the Canterbury area.

The consistency of the data also suggests that the sampling methods used give a satisfactory picture of the population level, where the collection of data is to be followed by transformation of the counts.

Introduction

A paper by Lowe and Dromgoole (1958) reviewed the methods recommended to that date for estimating or counting numbers in population studies of small insects. It also described an electronic machine designed to make counts from individual plants carrying heavy populations of the cabbage aphid. The designing of this device was part of the background work for a long term study of the dynamics of populations of this aphid on field crops in Canterbury.

The sampling work described in this paper is a further part of this background work designed to provide a basis for correct statistical procedures in the elucidation of the relationships between weekly population and the various factors governing the rise and fall of the population. Statistical procedures, such as analysis of variance, were devised for continuous variables, normally distributed with equal error variances. Insect counts usually differ from these variables in three ways; they are discrete, they have a skew distribution, and their variability rises with the size of the count. With the high average counts of aphids encountered here, the first difference due to discreteness may be ignored usually. The other two differences may be eliminated by transforming the counts, but it is unlikely that both differences will disappear under the same transformation although the elimination of one difference usually also reduces, rather than increases, the other difference. Since non-normality must be extreme to invalidate the analysis of variance it is better to concentrate on stabilising the variance of the samples.

METHODS

Field Sampling

To make possible inter-varietal comparisons both within and between seasons, the whole plant was chosen as the sampling unit, and it was ultimately proposed to undertake intensive sampling at weekly intervals on replicated plots at several sites, with only limited manpower available for making and recording counts.

In New Zealand this aphid overwinters as apterous females, and the samples referred to herein were drawn from natural populations in farmers' plantings of chou moellier, covering the spring rise in population from mid-August to November in each of several years. This period offers a population trend with countable samples, but wide variations between sets of samples, and is relatively uncomplicated by parasitism, predation, and disease.

First counts were made in 1955, and since at that time visual counting was the only accurate method available, this was used for all counts recorded here. In the main two operators were used, and where other operators were available, and made use of, their counts were tested for difference before being included in the sampling data. Table 1 lists the areas in Canterbury from which these data were drawn, and indicates the numbers of plants sampled in each set of data used, and the numbers of sets of samples consecutively drawn, usually at weekly intervals, in each area.

TABLE 1—Source of Data and Size of Samples

Area	Number of Sample Plants in Set	Number of Sets
Aylesbury	6	24
	12	23
	29	1
	31	1
	35	1
Darfield	5	105
	10	4
Hinds	12	13
Methven	12	10
Total	1332	182

All samples were taken at random on a paddock transect, except the 105 sets shown from Darfield, which were similarly drawn from adjacent small plots measuring half a chain square. In the main, counts were made and recorded in the field, though occasional heavily populated samples, or adverse weather, caused particular samples to be bagged and later counted in the laboratory.

Statistical Procedure

The small size (5–36) of the sets of samples is further reason for preferring stabilisation to normalisation in this data. There are enough sets of samples to determine the relation between mean and variance but individual sets are too small to give more than a vague indication of the true distribution of aphid counts. For this reason Spiller's (1952) method is also inapplicable.

If the relation between m and variance v of a set of counts is

$$v = f(m)$$

the transformation $g(c)$ of the count c which stabilises its variance is (Kendall, 1948)

$$g(c) = \int^{c} [f(m)]^{-\frac{1}{2}} dm$$

the value of the stabilised variance being unity. As confirmation, all counts may be transformed according to $g(c)$, m and v recomputed for each set of counts and the graph of the new values of v against m checked for independence.

RESULTS

The graph of the variances against the means of the 182 sets of counts showed a curvilinear trend that suggested a power relation. On logarithmic paper (Fig. 1) the points lie very close to a straight line. Fitting a line is complicated by the presence of error in both variables. The usual regressions taken each way have slopes of 1·70 and 1·63 between which limits the best regression slope must lie. If the insects followed the common negative binomial distribution in each sample the error variance of the log variance would have been about six times the error variance of the log mean. In this case Wayman's (1959) method gives a regression equation of

$$\log v = 1{\cdot}647 \log m + 0{\cdot}5336$$

so that

$$v = 3{\cdot}417 m^{1{\cdot}647}$$

is the relation between mean and variance. Even if the insect distribution is not quite negative binomial in samples the best estimate of the relation between mean and variance cannot differ greatly from this and we will take it to be

$$v = 3{\cdot}42 m^{1{\cdot}65}$$

for the rest of this paper.

The analysis was taken a stage further by separating the counts from the four areas in Table 1, which had mean counts of 408, 26, 135, and 10 respectively. In spite of the wide differences between these means the regressions within these areas do not differ significantly either from each

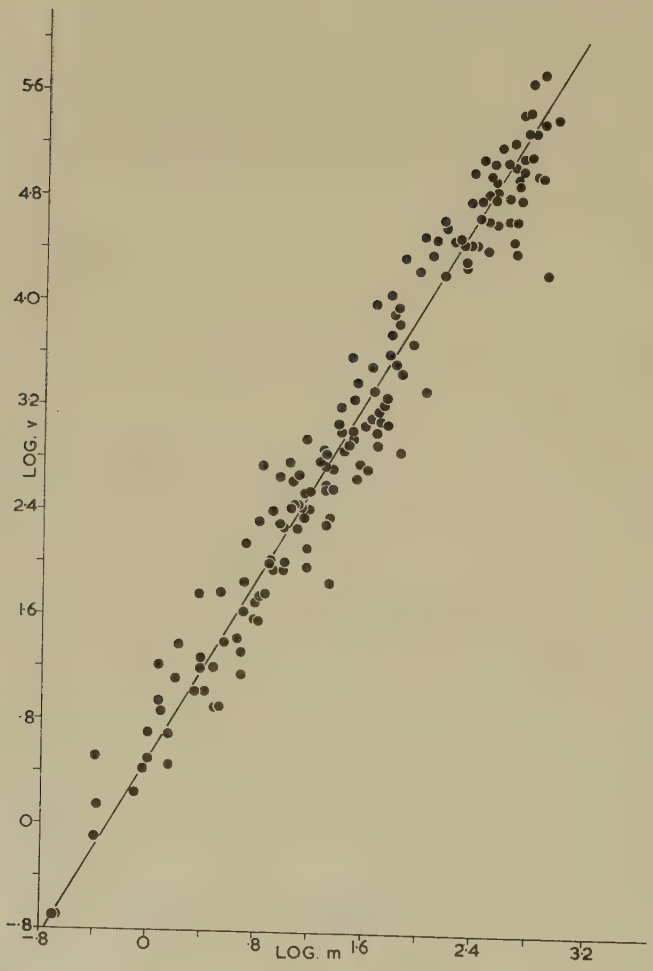

FIG. 1—Graph of variance against mean of 182 sets of aphid counts.

other or from the regression between the four areas. There is no evidence that the observations do not form a homogeneous set characterised by a common relation between the mean and variance of sets of counts.

The transformation which stabilises the variance is then

$$g(c) = c^{0\cdot175}$$

with a stabilised variance of 0·105. The counts were transformed in this way, and the means and variances recomputed and plotted in Fig. 2.

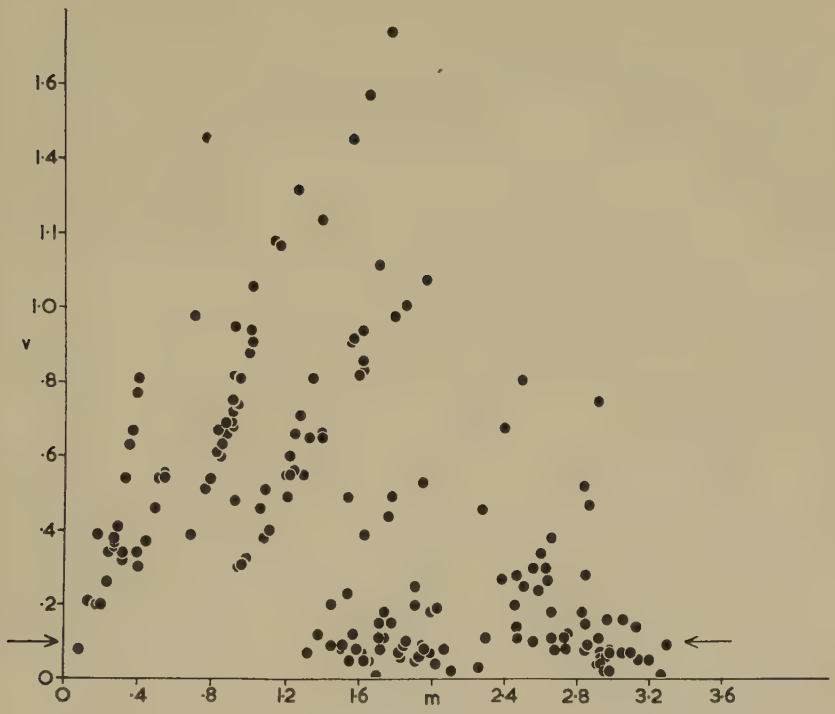

FIG. 2—Graph of variance against mean of 182 sets of aphid counts transformed by $c^{0.175}$

DISCUSSION

The commonest ecological models are the contagious distributions which include the negative binomial. They arise either from contagion (familial or social grouping) or from the mixing of different random distributions. Pruess and Weaver (1959) fitted one of these distributions to counts of the clover root borer, Beall (1941) did the same for the corn borer, the Colorado beetle and the tobacco wireworm and Bliss and Fisher (1953) for the European red mite, the corn borer, the beet leafhopper, the wireworm, ticks and isopods as well as some bacteria and plants.

Our data comprise samples from 182 distributions. These samples are all too small for individual comparison with models in the above manner and the only property that we have determined is the relation

$$v = 3{\cdot}42m^{1{\cdot}65}$$

between the mean and the variance of the sets of counts. This is in contrast to the relation in contagious distributions

$$v = m + m^2/k$$

However, this is not evidence against a negative binomial distribution for cabbage aphids in individual samples. With our wide range of sample means the parameter k may vary with m in such a way as to imply our relation between v and m. This is to be the subject of a further investigation and does not concern us here. The transformation consequent on our relation between the mean and variance is the fractional power transformation $c^{0.175}$.

The success of this transformation is shown by Fig. 2 in which the mean and variance of the transformed counts are clearly unrelated. An anomaly, however, is the high value of many of the variances compared with the expected variance indicated by the arrows in Fig. 2. Most of these high values arise from sets containing some zero counts. Some anomaly may be expected to arise in transforming such sets because the theory of the transformation is valid strictly only for large counts although it does happen to be satisfactory for small non-zero counts. Fortunately another consideration shows that the variances are in fact stabilised but at a higher level of variance than anticipated.

The ratio between the extreme values in this collection of 182 variances is $r = 290$. Then $z = \frac{1}{2}\log_e r = 2{\cdot}8$ is the maximum value of z in this collection. z is approximately normally distributed with variance $\sigma^2 = 1/f$, when f is the number of degrees of freedom of a variance; on average $\sigma^2 = 5{\cdot}1$. The expectation of a range in a normal distribution is about $\sigma n^{\frac{1}{2}}$ (Masuyama, 1957) where n is the size of the sample supplying the range. The expected range of z is then $(182/5{\cdot}1)^{\frac{1}{2}} = 6{\cdot}0$ and the expected maximum value of z must be 3·0. Evidently the variances of the transformed data are correctly stabilised.

Although this fractional power stabilises the variance better than any other transformation it is worthwhile investigating how much worse other transformations may be. Three other transformations were tried.

Kleczkowski (1949) suggests the transformation $\log(c + k)$. Applied to our data this transformation induces a unimodal relation of variance to mean. The minimum values of variance are at the highest and lowest values of the mean and they are equalised in our data if $k = 0{\cdot}35$. This suggests a transformation so near to the common $\log(c + 1)$ that the latter only was tried. With this low value of k the mode was so near the lower end of the curve as to be indistinguishable and indeed the graph of variance against mean of the transformed counts was very like Fig. 2 which was derived from the fractional power transformation.

The transformation $\log(c + 40)$ was also tried to test the sensitivity of the $\log(c + k)$ transformation to change in k. The value of 40 for k should place the mode of the relation between mean and variance at about the mean of the 182 sets. In this case the counterpart of Fig. 2 revealed a parabolic type of relation between mean and variance and clearly failed to stabilise the variance.

The relationship $v = m + m^2/k$ for a contagious distribution leads to the inverse hyperbolic sine transformation $k^{\frac{1}{2}} \sinh^{-1}(c/k)^{\frac{1}{2}}$. In our data k must be variable and there was some evidence that most of its variation was between, rather than within, the four areas listed in Table 1. Values of 1·27, 0·49, 0·66, and 0·03 respectively were used to transform the counts

in each area. For large counts this transformation becomes $\log(c + \frac{1}{2}k)$ which is close on the average to the previous $\log(c + 0{\cdot}35)$. Once again the counterpart of Fig. 2 was similar to Fig. 2 itself.

The distributions of the transformed counts were compared with each other and with the original counts and with the expected normal distribution by means of the ratio, r, of maximum to minimum variance of a set of counts. Table 2 contains r and also $z = \frac{1}{2}\log_e r$ which we have shown to have an expectation of 3·0 in a normal distribution. The last column shows that $\log(c + 1)$ and the inverse hyperbolic sine stabilise the variance as well as $c^{0{\cdot}175}$. All three produce the expected range of variance.

TABLE 2—Comparison of Variance Range of Observed and Several Transformed Counts with Expectation

Transformation	Ratio, r, of Extreme Variances	Maximum $z = \frac{1}{2}\log_e r$
Observed	$6{\cdot}2 \times 10^6$	7·8
$\log(c + 40)$	7700	4·5
$\log(c + 1)$	410	3·0
$k^{\frac{1}{2}}\sinh^{-1}(c/k)^{\frac{1}{2}}$	360	2·9
$c^{0{\cdot}175}$	290	2·8
Normalised		3·0

CONCLUSIONS

Statistical

With so little to choose between these three transformations on statistical grounds the choice can be made on other grounds. $\text{Log}(c + 1)$ is a familiar transformation based on readily available tables. The inverse hyperbolic sine contains a parameter k which must be estimated and is not tabulated over the full range of k. The fractional power is not tabulated at all. Ease of computation then suggests that $\log(c + 1)$ is the best transformation to stabilise the variance of these aphid counts.

Field Sampling

The statistical examination of this data, collected by different but experienced operators, from different sizes of plots and paddocks, at various levels of aphid populations, has shown a consistent relationship between mean and variance. It may safely be concluded therefore that the sampling system used is a satisfactory one where collection of samples is to be followed by statistical examination of the data, and the recommended transformation used.

ACKNOWLEDGMENTS

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A GLASS WATER STILL WITH AUTOMATIC HEATING SWITCH

By C. B. Wright, Ruakura Animal Research Station, Department of Agriculture, Hamilton.

(Received for publication, 23 February 1961)

Summary

An efficient electrically-heated glass water still for distillation of water of high silica content is described.

Introduction

The need for a number of water stills located in separate chemical units at this station led to the trial of the all-glass still described by Ballentine (1954). This still, like commercially available stills previously used, had a number of disadvantages for local use. Owing to the high silica content of Hamilton water a hard flaky deposit formed in the boiler, blocking the constant level device, and making it necessary to clean the boiler vessel frequently. The bare nichrome wire, which burned out very quickly, contravened wiring regulations for 240 V supply. The reaction kettle used for the boiler was an expensive dollar item, and the design did not incorporate an automatic cut-off controlled by the condenser water. The still described here incorporates features which overcome these disadvantages.

Details of Construction

Base Board

A 9 in. × 1 in. board 4 ft long, to which the support block is attached by a metal angle bracket.

Support Block (1, Fig. 1)

An aluminium block 3 in. long, 3 in. dia. A cavity 2½ in. deep, 2 in. dia. is machined in this. A hole 1 in. dia. is drilled through the top and threaded to take a short tube to which the splash head is fixed by a rubber sleeve. In the side of the block, a hole is cut, large enough to take a standard domestic water jug fitting. Three bolts (2, Fig. 1) are screwed to the side and these hold the boiler by small angle pieces. A neoprene gasket has proved satisfactory.

Heating Element (3, Fig. 1)

An immersion heater, 1,500 watts, with the top bent at right angles and soldered to a domestic water jug fitting. This modification was originally made by an immersion heater manufacturer, but it can be done in the laboratory workshop.

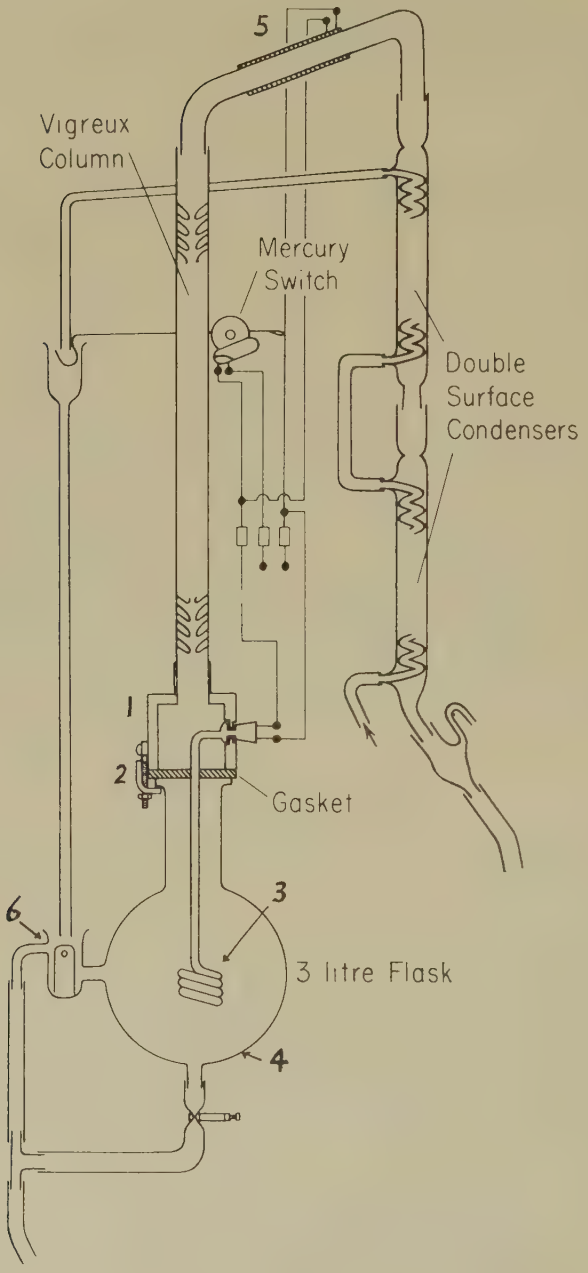
5
Vigreux
Column
Mercury
Switch
Double
Surface
Condensers
1
2
Gasket
3
6
3 litre Flask
4

FIG. 1

BOILER (4, Fig. 1)

A 3 l. bolt-neck flask with a constant level fused to the side, and a tubulature fused to the bottom. This tubulature, connected by a T-piece to the overflow waste pipe as shown, enables the boiler to be emptied every night by simply opening a screw clip. If this is done regularly no further cleaning is needed.

SPLASH HEAD

A Vigreux type column 4 ft long, fitted at the top with a B 24 socket. Only 12 in. at the top needs to be indented. The turnover has B 24 cones at each end and is wrapped with a suitable low wattage element (60 watt). This element keeps the internal walls above 100°C and prevents creep along this length of tube. (5, Fig. 1.)

CONDENSERS

Quickfit double surface type 12 in.–14 in. proved satisfactory. The condensers, splash head, and constant level delivery tube are fixed to the base board with spring clips.

CONSTANT LEVEL DEVICE

The device shown (6, Fig. 1) proved to be the most satisfactory of several tried. The connection between the constant level and boiler flask can be quite large (15 mm to 18 mm), and consequently strong, provided a sealed tube is fitted closely inside the vertical section. A small hole near the top of this tube allows air to escape. This arrangement provides sufficient pre-heated replacement water without allowing too much to enter and cause loss of boiling water down the overflow pipe.

ELECTRICAL CUT-OUT

A mercury switch is mounted on a simple balance arm using a small ball-race pulley as a pivot. A small cup at one end of the arm has a $\frac{1}{8}$ in. hole drilled in the bottom and is counterweighted so that when the cup is empty the mercury switch is open. This cut-out is simply made and fitted and has proved reliable.

OPERATION

The boiler is filled initially through the overflow pipe by opening the screw clip below the tubulature and connecting the pipe to a water supply. When the element is covered, the overflow pipe is let free and the screw clip tightened. Condenser water is turned on and when the boiler reaches its working temperature the flow should be reduced so that the outflowing cooling water is as hot as possible without loss of steam from the condenser.

PERFORMANCE

Measurements of the distilled water output for two stills equipped with 1,500 watt heating elements, and of the operating conditions, are as follows:

	Still A	*Still B*
Temperature of mains water	18°C	21°C
Temp. of water entering constant level	85°C	39°C
Volume of cooling water discharged	18 l/hr	40 l/hr
Distilled water output	1·8 l/hr	1·7 l/hr

Analysis of mains water: Total solids, 130 p.p.m.; SiO_2, 32 p.p.m.
Resistance of distilled water: Over 1×10^6 ohms per cm.

Six of these stills have been operating at this Station for over 12 months, some in daily use. Apart from replacement of the heating element after about 9 months, very little maintenance has been required, provided the boiler is emptied daily.

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FURTHER NUTRITIONAL STUDIES OF *Phytophthora cactorum*

By T. Christie, Cawthron Institute, Nelson.

(Received for publication, 23 November 1960)

Summary

The near-optimum level of calcium nitrate as the source of nitrogen for growth of the fungus *Phytophthora cactorum* was 1·90 g per 1,000 ml. Glucose as the source of carbon at this level of nitrogen gave similar yields between and including 7·50 g and 120 g per 1,000 ml. Increasing the level of calcium nitrate depressed growth. Glucose at a concentration in excess of 120 g per 1,000 ml also depressed growth.

Six amino acids, dl-tyrosine, dl-aspartic acid, dl-threonine, l-glutamic acid, dl-citrulline and dl-serine, stimulated the growth of the fungus when added to a medium in amounts sufficient to bring the total nitrogen to the same level as in a basal medium. Added asparagine and l-hydroxy-proline neither significantly stimulated nor depressed the growth of the fungus. All remaining amino acids significantly depressed growth.

Introduction

In a previous examination of the utilisation of nitrogen and carbon compounds by *Phytophthora cactorum* (Christie, 1958), a synthetic medium was used containing calcium nitrate at a level of 3·80 g per 1,000 ml and glucose at a level of 30 g per 1,000 ml. Since no information was available of the optimum levels of these compounds for the growth of this fungus, a study was made of the response of the fungus to varying quantities of both compounds. It was also deemed of interest to determine the growth response of the fungus in the synthetic medium to the addition of single amino acids.

Materials and Methods

The basal medium, $Ca(NO_3)_2$, 3·80 g; KH_2PO_4, 2 g; KCl, 0·5 g; $MgSO_4 \cdot 7H_2O$, 0·5 g; glucose 30 g; distilled water, 1,000 ml; and thiamine hydrochloride, 25 p.p.m., was the same as used previously (Christie, 1958, 1959). Methods of inoculation and determinations of growth were also the same. All media tested for growth were adjusted to pH 6·0 and pH determinations were made at the end of the growth periods.

Growth at Different Levels of Nitrogen and Carbon

The quantity of calcium nitrate as a source of nitrogen was varied in the basal medium in amounts from 0·06 g to 11·40 g per 1,000 ml. At each level of calcium nitrate glucose was used as a carbon source in amounts from 1 g to 200 g per 1,000 ml. At a higher level of glucose (250 g/1,000 ml) only a trace of growth took place and at still higher levels no growth occurred. At a high concentration of calcium nitrate (30·40 g/1,000 ml) no growth was made by the fungus.

The growth of the fungus in the media is shown in Table 1. Growth is represented by the dried weight of mycelium in milligrams.

TABLE 1—Growth of *P. cactorum* with Varying Levels of Calcium Nitrate and Glucose

$Ca(NO_3)_2$ (g/1,000 ml)	(Glucose g/1,000 ml)													
	0	1	2	5	7.50	15	20	30	60	90	120	150	175	200
0				no growth										
0.06		10	10	35	32	28	32	21	26	18	17	8	7	2
0.12		13	28	32	42	51	38	40	38	48	34	28	9	5
0.24		7	37	48	62	70	70	72	54	46	54	51	41	
0.48		12	52	55	67	75	96	82	91	64	58	67		16
0.96		15	51	77	110	105	102	95	103	117	95		43	
1.90		18	51	118	137	152	155	148	135	144	143	90	54	17
3.80	no growth	20	44	90	120	119	128	137	127	123	123	33		
11.40		4	36	81	69	103	122	125	132	136	120	40	45	7
16.00		2		3		2		5						

The above data indicate the ability of the fungus to grow with calcium nitrate as a nitrogen source over a wide range of concentrations. At the lowest nitrogen level growth was relatively uniform over a range of glucose concentrations from 7·50 g to 120 g per 1,000 ml. With higher concentrations of glucose growth was reduced. Concentrations below 5 g also depressed growth. This same pattern of growth with different levels of glucose was shown at higher levels of calcium nitrate up to and including 3·80 g per 1,000 ml.

The optimum concentration of calcium nitrate appears to be near the level of 1·90 g per 1,000 ml. Doubling this concentration brought about a decline in growth. Higher concentrations still further reduced growth.

Growth in a Medium With the Addition of Single Amino Acids

In this study of the effect upon the growth of the fungus of amino acids the constituents of the basal medium were the same as used previously. Calcium nitrate was present in the basal medium at a concentration of 3·80 g per 1,000 ml and glucose at 7·50 g per 1,000 ml. In each medium containing a single amino acid calcium nitrate was present at the near optimum level for inorganic nitrogen, 1·90 g per 1,000 ml, and glucose at the same level as in the basal medium. Each amino acid was used in a quantity sufficient to bring the total nitrogen in each medium to the same level as in the basal medium. The purpose of this was to compare directly with the effect of the excess inorganic nitrogen in the basal medium, which was known to have a depressing effect upon growth, any stimulating or depressing effect of the added organic nitrogen as represented by each amino acid. All amino acids were of B.D.H. manufacture.

The dried weight of mycelium yielded by the fungus with each amino acid is shown in Table 2. Each amino acid was tested twice with five replicates in each trial. The maximum standard error determination did not exceed $\pm$ 9 mg.

Discussion

Only six amino acids, dl-tyrosine, dl-aspartic acid, dl-threonine, l-glutamic acid, dl-citrulline and dl-serine, had a significant stimulatory effect upon growth. The t-test was used to determine significance. Growth with asparagine and l-hydroxyproline was comparable with that in the basal medium. All other amino acids significantly depressed growth.

On the basis of results obtained from a grouping of amino acids according to the frequency with which they have been reported to be "good", "fair" or "poor" sources of nitrogen, Pelletier and Keitt (1954) loosely classified amino acids as follows: "good" sources of nitrogen: alanine, arginine, aspartic acid, glutamic acid, glycine and proline; "fair": histidine, isoleucine, serine, tyrosine and valine; "poor": cystine, hydroxy-proline, leucine, methionine, phenylalanine, threonine and tryptophan. Although the present study was not concerned with amino acids as sources of nitrogen, and in the absence of a substrate of inorganic nitrogen their effect upon growth may have been

different, a correspondence is shown between those which stimulated growth and those classified by Pelletier and Keitt as "good" or "fair" sources of nitrogen. Similarly those which depressed growth agree well with those classified as "poor" sources of nitrogen.

TABLE 2—Growth of *P. cactorum* in a medium with amino acids added singly

Added Amino Acid	Weight of Mycelium (mg)
dl-tyrosine	219
dl-aspartic acid	175
dl-threonine	171
l-glutamic acid	169
dl-citrulline	155
dl-serine	154
asparagine	132
basal medium	129
l-hydroxy-proline	126
glycine	107
dl-alanine	99
dl-phenyl-alanine	92
l-histidine	92
d-arginine HCl	90
l-arginine HCl	87
l-proline	81
dl-tryptophan	50
dl-ornithine HCl	47
dl-iso-leucine	44
dl-leucine	43
l-leucine	42
l-lysine	42
dl-methionine	41
l-cysteine HCl	26
dl-2-amino-n-butyric acid	22
l-cystine	21
dl-valine	20
dl-norleucine	16

The grouping of the above amino acids according to their stimulating or depressing effect upon growth in no way follows the classification of amino acids into "essential" and "non-essential", glycogenic or ketogenic, for the nutrition of higher animals. The amino acids which stimulated the growth of the fungus are those containing hydroxy, dicarboxylic and keto groupings, rich in oxygen. Of the imino acids hydroxyproline similarly had a greater effect upon growth than proline. Amino acids rich in nitrogen, histidine, arginine, ornithine and tryptophan, depressed growth. Amino acids containing sulphur markedly depressed growth.

At the end of the growth period all media were more acid than at the beginning. The shift in pH with the majority of the amino acids was from pH 6·0 to pH 5·0. For the six amino acids which stimulated growth pH readings at the end of the growth period were: dl-tyrosine, 5·2; dl-aspartic

acid, 5·8; dl-threonine, 5·6; l-glutamic acid, 5·8; dl-citrulline, 5·8; and dl-serine, 5·6. A smaller increase in acidity was shown with these amino acids than with those which depressed growth.

The growth response to the two isomers of arginine, d-arginine and l-arginine, was similar. Nor was there any difference between the effect upon growth of dl-leucine, l-leucine and dl-iso-leucine.

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AN INDICATION OF THE PRESENT RESISTANCE TO INSECTICIDES OF THE HOUSEFLY (*Musca domestica* L.) IN NEW ZEALAND

By A. G. SMITH, Plant Diseases Division, Department of Scientific and Industrial Research, Auckland.

(Received for publication, 13 February 1961)

Summary

Tests on a population sample of houseflies have revealed that houseflies resistant to dieldrin and lindane are present in New Zealand and that resistance to DDT has reached a very high level. There is no evidence of resistance to organophosphorus compounds.

INTRODUCTION

The most recently published report to note the state of resistance in a housefly population in New Zealand showed that by 1949 there were houseflies present which had developed a marked resistance to DDT (Harrison, 1951). Since then resistance to other insecticides besides DDT has had time to develop. The tolerance of houseflies to DDT, dieldrin, lindane, malathion diazinon and gusathion in a population sample is given to indicate the present situation.

TECHNIQUE

Houseflies were collected from four Auckland suburbs in mid-1959 (strain R) and at the same time an insecticide-susceptible laboratory strain (strain S) was obtained from Australia for purposes of comparison. Both strains were bred in the laboratory for several generations in a manner described by Smith (1961).

Flies required for testing were sexed and collected into batches of ten. Males were treated when 2–3 days old, females when 3–4 days old. Flies were given access to food until a few seconds before treatment. A 1 mm^3 dose of an acetone solution of insecticide was topically applied to the ventral thoracic surface of each fly. This was done by means of a ratchet controlled micrometer driven syringe, while flies were immobilised with CO_2. Three batches of flies were treated at each of the five concentrations for each insecticide, and acetone alone was used for the controls. After treatment the flies were held for 24 hr at 25°C. when mortality counts were made. Recovery cages consisted of petri dishes each containing a filter-paper and a supply of sugar-milk powder-water paste.

The topical application method was chosen for these tests for the following reasons. Firstly, a cuticular deposit was considered to approximate more closely to conditions of normal field practice than did treatment by injection. Secondly, it is possible to apply, with the topical application method, a closely controlled dose in a replicable situation on every fly. This cannot be done using residual deposits or space-spray methods of treatment. Finally, satisfactory results can be obtained by this method, without the use of large numbers of flies.

TABLE 1—Response of Two Strains of Houseflies to Topical Applications of Six Insecticides

Insecticide	Strain	Sex	LD50 in μg per Fly With 95% Confidence Limits in Brackets	LD50 Ratio Strain R / Strain S	Slope	Significance*
DDT	S	♂	0.026 (0.022–0.032)	190	3.66	N.S.
	R	♂	4.90 (3.92–6.12)		2.51	
	S	♀	0.047 (0.040–0.054)	340	5.53	N.S.
	R	♀	15.8 (12.8–19.4)		2.86	
Dieldrin	S	♂	0.0082 (0.0074–0.0091)	28	4.70	XXX
	R	♂	0·23 (0·15–0·33)		0.99	
	S	♀	0.013 (0.011–0.016)	26	6.41	XXX
	R	♀	0.34 (0.22–0.51)		0.90	
Lindane	S	♂	0.0057 (0.0046–0.0070)	33	3.99	X
	R	♂	0.19 (0.14–0.26)		1.96	
	S	♀	0.011 (0.0086–0.013)	88	4.29	XX
	R	♀	0.97 (0.70–1.36)		1.92	
Malathion	S	♂	0.074 (0.062–0.087)	2	4.23	N.S.
	R	♂	0.16 (0.14–0.19)		4.65	
	S	♀	0.16 (0.13–0.18)	1	5.23	N.S.
	R	♀	0.18 (0.16–0.21)		6.26	
Diazinon	S	♂	0.023 (0.019–0.028)	5	3.45	N.S.
	R	♂	0.12 (0.093–0.15)		2.46	
	S	♀	0.11 (0.092–0.13)	3	3.84	N.S.
	R	♀	0.31 (0.26–0.37)		3.44	
Gusathion	S	♂	0.036 (0.032–0.040)	2	5.01	N.S.
	R	♂	0.058 (0.049–0.069)		3.65	
	S	♀	0.055 (0.049–0.062)	3	4.64	N.S.
	R	♀	0.18 (0.16–0.21)		4.43	

*For significance of difference between slopes of R and S strains: N.S. indicates not significant. X indicates significant at 0·05. XX indicates significant at 0·01. XXX indicates significant at 0·001.

Acetone was used as the carrier because both chlorinated hydrocarbons and organophosphorus compounds are readily soluble in it. Further, acetone evaporates quickly so that treatments dry before the flies have time to recover fully from the effects of the CO_2 and this minimises subsequent loss of insecticide through contacts.

RESULTS

Results of LD50s in micrograms per fly are given in Table 1. The LD50s, with 90% confidence intervals and slopes of the dosage-response curves were calculated using Karber's method (Cornfield and Mantel, 1950).

Batch weighings made at testing time, for strain S averaged 20 mg for females and 14 mg for males. Strain R averaged 21 mg for females and 17 mg for males.

DISCUSSION OF RESULTS

The LD50 results show that in strain R resistance is highly developed to DDT and well marked to dieldrin and lindane. Strain R appears to have general susceptibility to the organophosphorus compounds. The slightly increased tolerances shown in comparison with strain S are considered insufficient to indicate that any real resistance to this group of compounds has yet developed.

The exact degree of resistance present is less clearly defined. Any scale used must be an arbitrary one as insecticidal results can vary according to the carrier used (Busvine 1951). Acetone was chosen for reasons already described and results obtained are therefore based on an acetone scale of resistance. From such a scale it is possible to determine if resistance is present or not and, from previous and subsequent tests using the same scale, whether it is increasing. Also it is possible to determine when resistance has developed to such a degree as to make the use of a certain insecticide impracticable as a means of control.

The slopes of the dosage – response curves indicate the range of variation of individual susceptibilities present in the population; the lower the slope the greater the variation. In a population containing a wide variation of susceptibilities there is every reason to expect a marked increase in general resistance to an insecticide if selection pressure is maintained.

A marked decrease in the slope is shown with dieldrin and lindane for strain R in comparison with strain S. It is therefore to be expected that general resistance to these two insecticides will increase.

ACKNOWLEDGMENTS

The author wishes to thank Mr R. W. Kerr, Division of Entomology, CSIRO, Canberra, for supplying the flies from which strain S was bred, and Dr H. R. Thompson, Applied Mathematical Laboratory, for carrying out the statistical analysis.

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NOTES ON BREEDING HOUSEFLIES (*Musca domestica* L.)

By A. G. SMITH, Plant Diseases Division, Department of Scientific and Industrial Research, Auckland.

(Received for publication, 13 February 1961)

Summary

A technique for housefly breeding involving the use of simple and easily assembled pieces of equipment is described. Formulae for adult and larval foods used with this equipment are also given.

INTRODUCTION

Continuous breeding of housefly colonies in the laboratory can be time consuming if equipment is not easy to maintain. The use of inexpensive readily available components which can be easily assembled and replaced is therefore an obvious advantage. The following technique has been used during the last year at this laboratory and found to be reliable.

EQUIPMENT AND TECHNIQUE

Adult Fly Cage

The adult fly cage (Fig. 1) consists of a cylinder of 12 mesh galvanised wire gauze 8½ in. in diameter and 17 in. in length closed at each end with a tin lid clipped in position. A hole at the centre of each lid coincides with a short length of copper tube soldered in position for the attachment of plastic bottles. Cages are hung skew from the ceiling of the breeding room so that any dead flies collect clear of the central hole in the bottom lid.

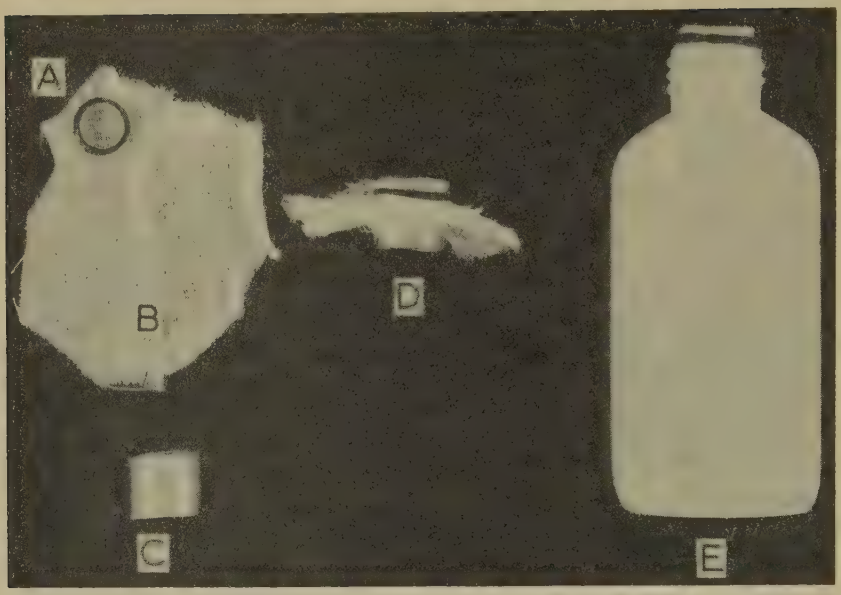
Feeding, Pupal Holding, and Oviposition

Four-ounce plastic bottles are used to supply food for adults, to hold pupae for emergence, and to supply oviposition sites. The bottles are held in place on the cage by means of their plastic screw caps which have had their tops cut off. The caps are permanently press fitted in the copper tubes on the ends of the cage.

Feeding Units

Each plastic bottle is filled with liquid food consisting of 100 ml water, 8 g powdered whole milk, 4 g sugar and 0·1 ml formalin. The neck of the bottle is then plugged with a feeding pad. The assembled feeding pad is shown in Fig. 2 (D) and its components in Fig. 2 (A, B and C). The complete feeding unit Fig. 2 (E) is then inverted and screwed into the top lid.

FIG. 1—Adult fly cage with two bottles fixed in position.



Photos by S. A. Rumsey

FIG. 2—A. Elastic band. B. Muslin cover. C. Polyvinylchloride tube. D. Feeding pad assembled. E. Feeding unit complete.

Pupal Containers

The bottles are no more than three-quarter filled with dry loosely packed pupae and provided with a strip of card to assist the escape of newly emerged flies into the cage. These bottles are screwed into the bottom lid.

Oviposition Units

Bottles used for oviposition are provided with a piece of muslin moistened with adult food plus a few drops of weak ammonium hydroxide as an added attraction to oviposition. A strip of card provides the flies with easy entry to and exit from the bottle. These bottles are screwed into the bottom lid for the period required for oviposition. The eggs obtained are readily separated and cleaned by half filling the bottle with water and shaking vigorously.

An accumulation of dead flies can provide an attractive alternative oviposition site to that of the bottle. In certain cases therefore when eggs are required from a cage containing many dead flies or one containing only a few young flies, another type of oviposition unit has been found more effective. This is situated within the cage and consists of a polythene cone 5 in. long and 3 in. in diameter at the open end. A stiff wire 5 in. long within the cone prevents it falling over and both wire and cone are held at the cone's apex in a split cork. The cone, which is provided with a piece of

muslin similar to that used in the oviposition bottle, is inserted into the cage through the hole in the bottom lid and held in place by the cork.

Larval Breeding

For larval breeding a medium similar to that used by Fisher and Jursic (1958) is used. It is contained in 2 lb straight sided glass preserving jars. The medium is prepared by mixing together 31·5 g powdered whole milk and 1·5 g dried yeast with 125 ml water. To this suspension is added 31·5 g absorbent tissue paper which is allowed to soak for half an hour when it can be easily pulped. This quantity of medium, enough for one jar, is teased out and seeded with 0·3 ml eggs (2,250 approx.). The jars are covered with an open weave fabric to enable the gases to escape freely.

Pupal Separation

Pupae are separated by floatation a day or so after pupation is complete. The top of the medium which contains no pupae and has a tendency to float is discarded. The rest of the medium and pupae are disentangled by stirring. Pupae are scooped off the surface of the water, drained and spread out to dry on a sheet of blotting paper. Pupae collected in this way are clean and undamaged.

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A FILTER ANALYSIS OF NEW ZEALAND ANNUAL RAINFALL

By J. F. DE LISLE, N.Z. Meteorological Service

(Received for publication, 29 November 1960)

Summary

The annual rainfalls at 108 stations in New Zealand were expressed as indices which were percentages of the 1911–40 means. A space-mean of the indices was found for six areas into which the country was divided and the six series from 1890 onwards analysed by a set of filters. The relation of the filtered outputs of the series of space-mean indices to that of individual station indices was found.

The fluctuations of periods $>$ 12 years in the three areas in the northern half of New Zealand were found to correlate with one another; the variances however were small. It is suggested that these were caused by a long-period fluctuation in the number of depressions affecting the North Island. No relations were found between other components from any of the areas.

The relation of these results to those on climatic changes in the subtropics found by Kraus is discussed.

INTRODUCTION

The question of the existence of long-period fluctuations in New Zealand's annual rainfall is of some interest because of comparisons which may be made with similar results found elsewhere and because of connections which may be found with long-period variations in the general circulation of the atmosphere. (See Kraus 1960.)

The problem was first treated by Seelye (1950) who summarised the annual rainfall at a selection of stations throughout New Zealand into annual indices which were percentages of the 1911–40 means. By averaging station indices he found mean annual indices for the North Island, the South Island, and for the whole of New Zealand. By a rough smoothing procedure the series of space-mean indices were separated into short and long fluctuations and by least squares a linear trend fitted to the 30-year running means of the long period components. A decreasing trend was found for the period 1863–1947 but the standard errors of the determination were large and, as Seelye stated, "the description of the slow movements of rainfall as a linear trend is an over-simplification."

The problem is re-examined here using filter methods (Craddock (1957), de Lisle (1957)) to split up the rainfall series into frequency bands of known width. The same stations as those used by Seelye were taken, the annual rainfalls of the individual stations being expressed as percentages of the 1911–40 mean.

Because the rainfall regimes in New Zealand are so varied the station indices were meaned over small areas. The six regions chosen, shown in Fig.1, were districts in which it was considered that the variation of a space-mean index would be approximately representative of the variation of the individual station indices.

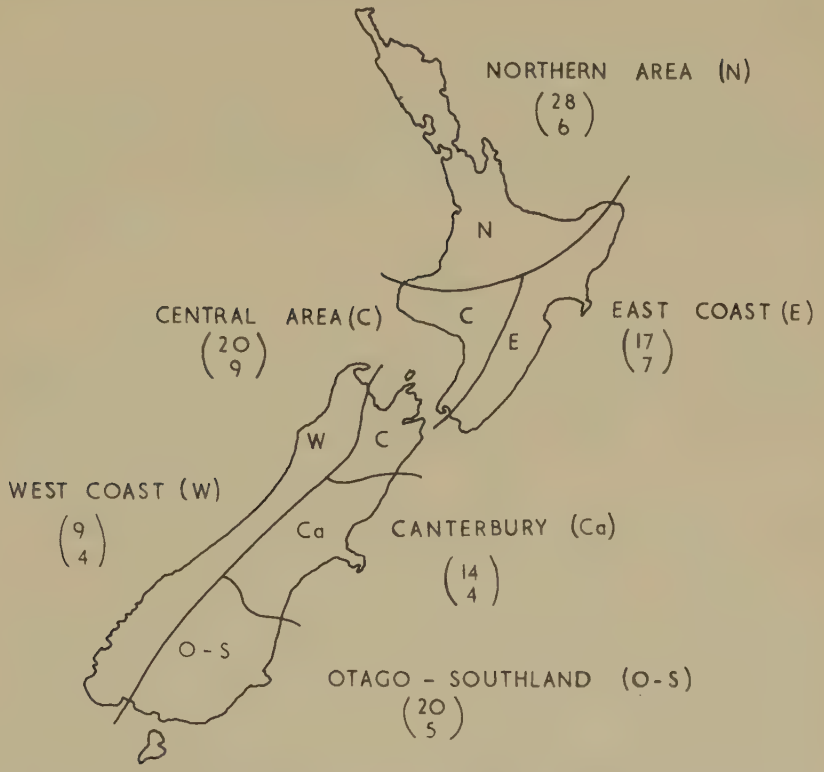

FIG. 1—Areas for which space-mean annual rainfall indices were calculated. Figures show the number of stations in each area. The upper figure in each pair is the number from 1911 onwards and the lower the number in 1890 except for the West Coast where the series starts in 1894.

Observations made prior to 1890 were not used because of the small number of stations then operating in each area. Even so, the number of stations available did not reach a maximum until about 1910 so that none of the series of space-mean indices is homogeneous. The largest and smallest number of stations used in each area are also shown in Fig. 1.

The mean annual indices for the six areas are listed in the appendix.

RELATION OF SPACE-MEAN TO INDIVIDUAL STATION INDICES

Because space-mean indices are to be analysed it is essential for interpretation of the results that the relation of the filtered output of a series of space-mean indices to that of a series of individual station indices be known.

Consider a number of rainfall stations in a homogeneous rainfall area. Let $(R_i)_t$ be the annual rainfall index at station i for year t and $\bar{R}_t$ the space-

mean index for the year t

Then $(R_i)_t = \bar{R}_t + (\varepsilon_i)_t$ .....(1)

were $(\varepsilon_i)_t$ is the difference from the mean.

In each of the areas considered here the ε were found to be approximately normally distributed with standard deviation given in Table 1. The frequency distribution of the ε for each area are shown in Fig. 2.

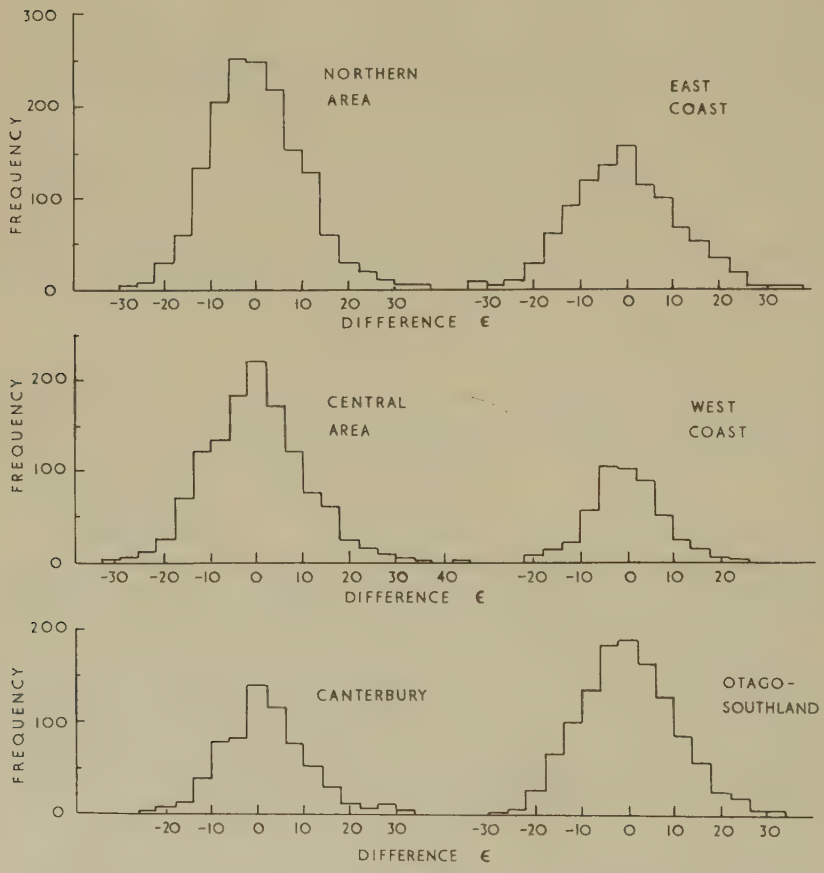

FIG. 2—Frequency distributions of ε the differences of individual station indices from the space-mean indices.

If in a particular rainfall area, the correlation between the ε at any station and the $\bar{R}$ is small, the $(\varepsilon_i)_t$ may be considered as a random sample from a normal population of standard deviation given in Table 1. In a random selection from the 108 stations used in the analysis little relation was found between ε and $\bar{R}$.

TABLE 1—Standard Deviations of Difference Terms ε

Area	N	E	C	W	Ca	O–S
S.D. of ε (%)	13.1	15.2	14.3	10.2	13.2	13.4

The filtered output y_t from a given series x_t is found by forming weighted running means.

$$y_t = \sum_j a_j x_{j+t}$$

where a_j the filter weights are designed to give any desired frequency response (see de Lisle (1957)). In the filtering process the amplitude of any harmonic component is multiplied by the response or gain function of the filter, but the phase and period are left unchanged.

Taking weighted running means of (1) we have

$$\sum_j a_j (R_i)_{j+t} = \sum_j a_j \bar{R}_{j+t} + \sum_j a_j (\varepsilon_i)_{j+t} \quad \text{.....(2)}$$

Now if a random sample from a normal population ε is harmonically analysed, it is easy to show that the variance of the amplitudes is independent of frequency, being given by $\frac{\text{Variance } \varepsilon}{N}$ were N is the number in the sample.

In a perfect band-pass filter in which the gain function $A(\omega) = 1$ for the frequency range $\omega_1 \leqslant \omega \leqslant \omega_2$ and $A(\omega) = 0$ for $\omega < \omega_1$ and $\omega > \omega_2$ the variances of the outputs of the ε_i terms in (2) can be found. Therefore in a rainfall area the filtered outputs of a series of station indices will lie somewhere within a zone of uncertainty about the output of the series of space-mean indices.

Here the filters are not perfect and the zones of uncertainty have standard deviations which vary from approximately 1·4% for the West Coast Area to 2% for the East Coast Area.

FILTER ANALYSIS

Because of the terms lost in the running mean process a compromise must be reached between the efficiency of the filter used and the number of useful terms left in the output series. A set of four 13 term filters was used here and the manner in which they cover the frequency range 0 to $\frac{1}{2}$ year^{-1} is shown by the response curves given in Fig. 3. The set is such that each filter has zero gain at the peak frequencies of all other members of the set. The weights and peak periods of each member of the set are given in Table 2. These are the same type of filters as those used by Craddock (1957).

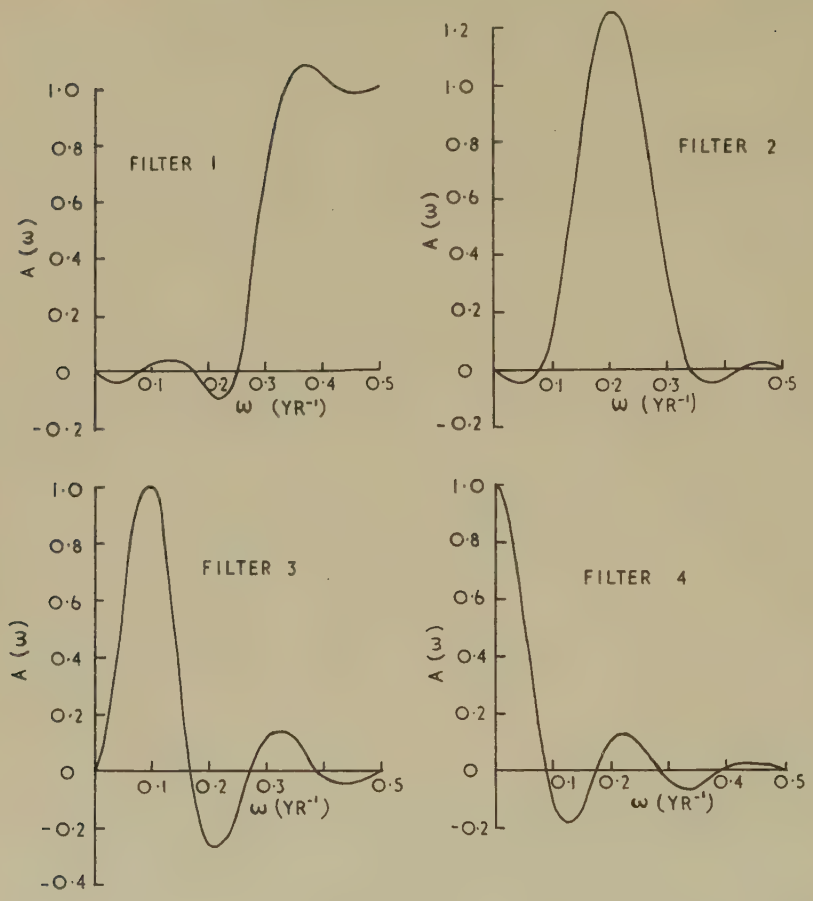

FIG. 3—Gain curves for the 13 term filters used. ω is frequency in year^{-1} and $A(\omega)$ the gain.

TABLE 2—Peak Periods and Weights of Filter Set

Filter No.	Peak Periods Years	a_0	Weights a_1 a_{-1}	a_2 a_{-2}	a_3 a_{-3}	a_4 a_{-4}	a_5 a_{-5}	a_6 a_{-6}
1	2, 3	0.4167	−0.6221	0.1667	0.1667	−0.1667	−0.0447	0.0833
2	4, 6	0.3334	0.1667	0.5000	−0.3333	0.1667	0.1667	0
3	12	0.1667	0.2887	0.1667	0	−0.1667	−0.2887	−0.1667
4	>12	0.0833	0.1667	0.1667	0.1667	0.1667	0.1667	0.0833

The set of four filters was applied to each of the six series of space-mean rainfall indices and the variances of the output series and of the original series were calculated. They are shown in Table 3.

TABLE 3—Variances of Original Space-mean Series and of the Filter Outputs. $(\%)^2$

Area / Series	N	E	C	W	Ca	O–S
Original Series	224.3	224.0	191.5	79.2	263.8	110.3
Filter 1	84.5	103.1	70.2	45.0	83.3	25.1
2	51.2	71.8	39.3	23.0	82.3	57.5
3	54.4	36.4	27.5	10.8	47.6	27.3
4	6.9	15.0	5.1	5.7	19.0	7.4

From Table 3 it is seen that in general the amplitudes decrease with increasing period of component and that the 2 to 3 year period components are largest except in the case of Otago-Southland. The longest period components have the smallest amplitudes and in no case does the variance exceed 7% of the variance of the original series.

To illustrate the phase relations of the longest period components, the outputs from Filter 4 are plotted in Fig. 4. This shows similarities in the phases of the most prominent fluctuations from the Northern, East Coast, and Central Areas. In the remaining South Island Areas the fluctuations are dissimilar from one another and from the North Island fluctuations. The small amplitude short-period fluctuations superimposed on the longer period movements in Fig. 4 are the result of the imperfect nature of the filter.

Craddock (1957) introduced the idea of "the equivalent number of degrees of freedom" of a filter and following Tucker (1957) we may write approximately

$$N_1 = 2N \frac{\left(\int_0^{\frac{1}{2}} A^2(\omega)\, d\omega \right)^2}{\int_0^{\frac{1}{2}} A^4(\omega)\, d\omega} \qquad \text{.....(3)}$$

where N_1 is the equivalent number of degrees of freedom

N the number of terms in the series to be filtered

$A(\omega)$ the gain function given by

$$A(\omega) = \sum_j a_j \cos 2\pi j\omega$$

In the derivation of (3) it is assumed that the original series is normal and that N^{-1} is small compared with the band width of the filter.

Knowing N_1 we can estimate the significance of the correlations between the filter outputs found from the application of the same filter to different

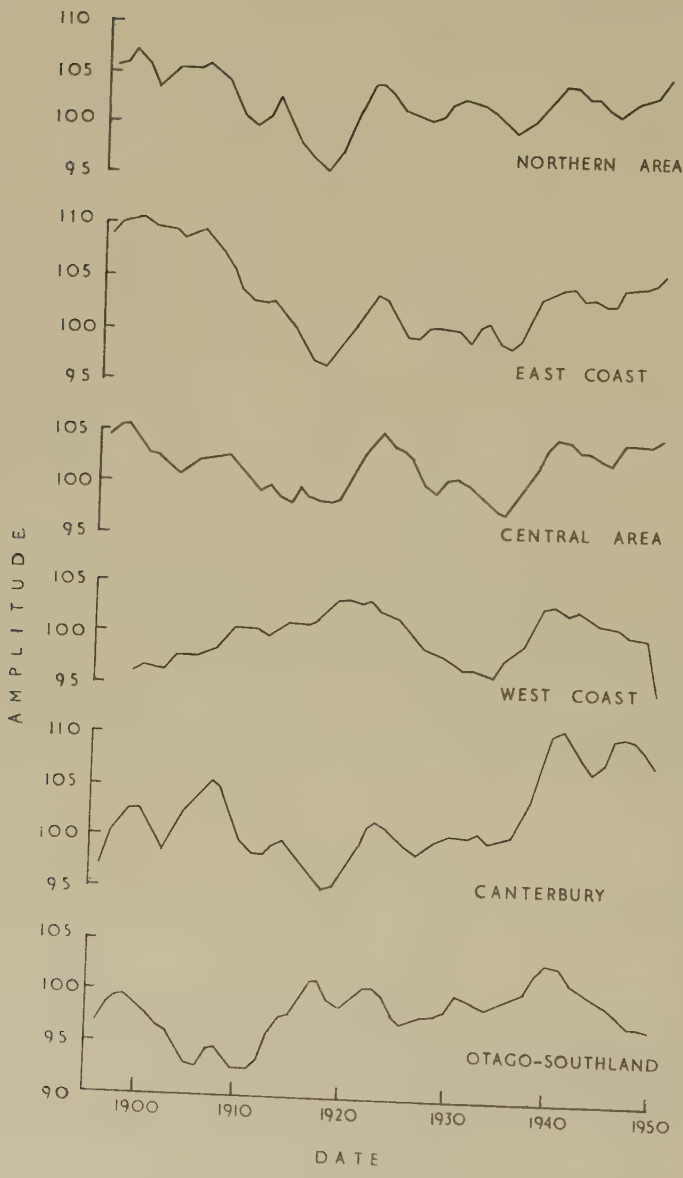

FIG. 4—Fluctuations of space-mean rainfall indices with periods > 12 years. Outputs from Filter 4.

original series. N_1 for Filter 4 was 20 and the correlations between the outputs of Filter 4 from pairs of the northern areas, N, E, and C together with confidence limits at the 5% level are given below.

Areas	N, E	E, C	C, N
Correlation	0.69	0.63	0.66
Confidence limits	0.35–0.87	0.26–0.84	0.30–0.85

While the above correlations are not high it must be remembered that the filters are imperfect and the space-mean series analysed are not homogeneous. The effect of filtering the same series with a more efficient filter is shown in Fig. 5 where a low-pass filter retaining all periods > 15 years is used. This has 29 weights in the running mean and loses 16 more terms in the filtering process than lost in using Filter 4. The outputs show quite clearly the phase correspondence in the long term components in the northern areas N, E, and C and the lack of correspondence in any of the other series.

There would thus seem to be similar long-period fluctuations (> 12 years) present in the annual rainfall series of the North Island and Marlborough (in the north of the South Island) for the years 1890–1956.

The outputs from Filter 3 with peak period 12 years are shown in Fig. 6. The most notable features of these outputs are the large amplitude regular fluctuations from the three northern areas and the marked correspondence of some of the fluctuations. However, the phase correspondence does not persist for the whole record as it does in the case of the longer period components from these areas.

The two bottom outputs in Fig. 6 also show some phase correspondence but again there is no overall similarity. The West Coast output on the other hand has quite a different character from any of the others.

Thus there does not appear to be a stable phase correspondence between any two areas in fluctuations with peak periods of 12 years. These components will not be further considered here.

The shorter period fluctuations, the outputs from Filters 1 and 2 are not displayed here. They showed somewhat similar features to those in Fig. 6 and there was no general correspondence in either phase or amplitude between the fluctuations from any two districts.

The question of the presence of a trend, or fluctuation whose period is long compared with the length of the record, can be settled by reference to the long-period outputs from Filter 4, shown in Fig. 4 and from the more efficient filter shown in Fig. 5.

In the three northern areas the long-period fluctuations are correlated so there is probably some long-period circulation change affecting all three districts. Any trend shown is not likely to be a statistical accident.

However, because of the general oscillatory nature of the outputs shown in Fig. 5 and the relatively large amplitudes of the fluctuations there is no

justification for attempting to fit a straight line. While it would be possible to fit a very flat parabolic curve concave upwards to the two upper graphs in Fig. 4, this certainly could not be extrapolated.

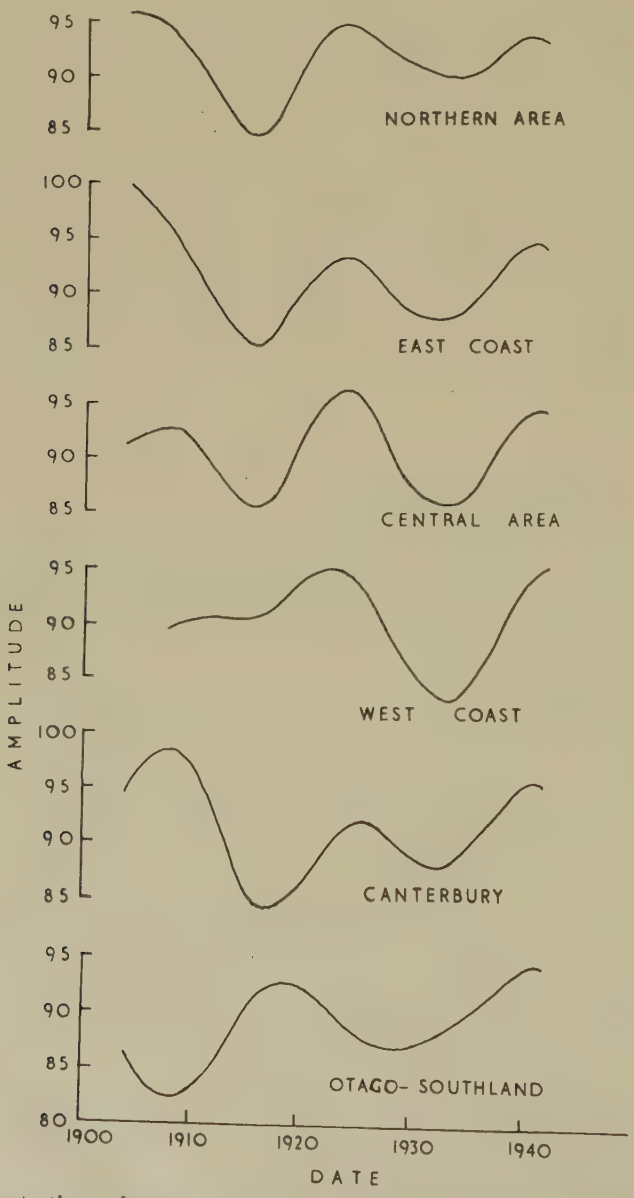

FIG. 5—Fluctuations of space-mean rainfall indices with periods > 15 years. Filter used is more efficient than Filter 4 whose output is shown in Fig. 4.

The dissimilar outputs from the three South Island areas would throw doubts on the reality of any trends shown in these series unless some physical reason could be advanced to account for them.

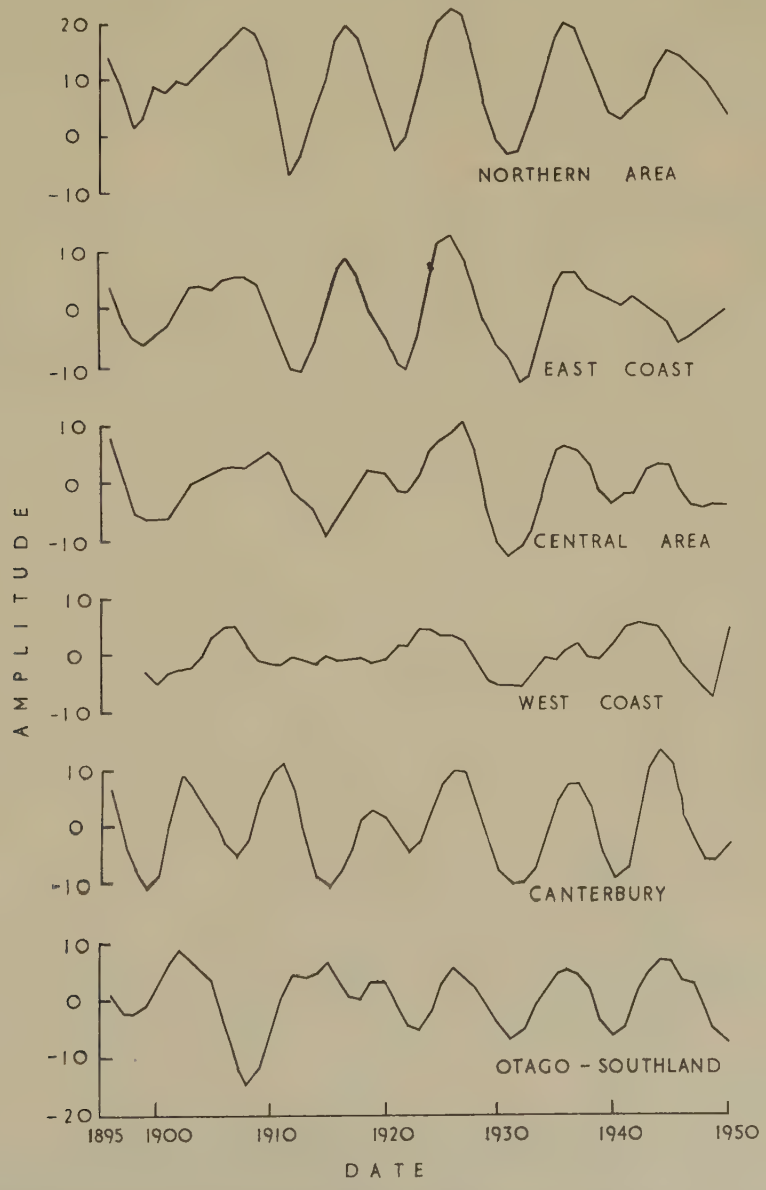

Fig. 6—Fluctuations of space-mean rainfall indices with peak periods of 12 years. Outputs from Filter 3.

The West Coast long-period fluctuation shows no trend at all. The amplitudes of the fluctuations in the Canterbury series show relative differences in the outputs from the two long period filters illustrated in Figs 4 and 5. This could be due to the small difference in cut-off period in the two filters.

The Southland fluctuations show a slightly upward tendency but because of the differences in the outputs from the two neighbouring areas Canterbury and Otago-Southland there appears to be no reason to doubt the random nature of the components.

LONG-PERIOD CIRCULATION CHANGES

To find a reason for the similarities in the long-period fluctuations of annual rainfall in the North Island some system must be found which produces more rain in the North Island than it does in the South Island.

If we consider the rainfall producing situations in New Zealand it is found that the South Island is throughout the year in the belt of mean westerly winds and rainfall is largely caused by troughs in the westerlies which may or may not affect the North Island. The North Island frequently comes under the influence of depressions which form in the North Tasman Sea or in the months November to March may be of tropical origin. These bring rain to the North Island more often than they do to the South Island.

It is plausible then that the long term variations in North Island rainfall are due to a long term variation in the number of depressions passing over or near the North Island. This effect is, however, very small, its variance accounting for less than 7% of the variance of the North Island rainfall.

An analysis of annual rainfall from a large number of both northern and southern hemisphere tropical and subtropical stations has been made by Kraus (1958) using cumulative percentage deviations from a long-term mean. He presented curves to show that precipitation in the subtropics was generally above the 1881–1940 mean during the latter half of the nineteenth century and a drier period set in during the 1890s. The changes were found on the Australian and North American east coasts to about latitude 40° but not in higher latitudes.

The long-period fluctuations found in the present analysis show a number of similarities with the results given by Kraus. Here we have,

(a) A decrease in the North Island rainfall from about 1898 to 1917 followed by a temporary recovery and a further fall before the rise in the mid 1930s.

(b) Except for a rise in all South Island districts in the late 1930s, no general changes of the rainfall in the higher latitudes of the South Island.

CONCLUSIONS

(1) The annual rainfalls at stations in the North Island and Marlborough have shown similar long-period fluctuations (Periods $>$ 12 years) since 1890. They are probably due to variations in the number of depressions passing over or near the northern half of New Zealand.

(2) The fluctuations are small and do not contribute more than 7% to the variance of annual rainfall.

(3) The three South Island districts all showed different long period fluctuations which are probably random effects.

(4) Fluctuations of shorter period components showed no overall correspondence in any of the six areas considered.

(5) In studying secular changes, the use of a space-mean index to specify the rainfall regime of larger areas than those taken here is permissible only when considering long period fluctuations from the northern half of New Zealand. In all other cases the rainfall regimes are too variable.

(6) The types of fluctuations found and the probable explanation in terms of circulation change agree with the results found by Kraus.

ACKNOWLEDGMENTS

Thanks are due to Mr B. C. Ereckson who supervised most of the calculations which were done on the I.B.M. machines of the Central Accounting Bureau, the Treasury, through the courtesy of the officer in charge.

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APPENDIX

MEAN ANNUAL RAINFALL INDICES

	Northern Area	East Coast	Central Area	West Coast	Canterbury	Otago-Southland
1890	108	90	86	..	63	76
1	89	91	81	..	75	92
2	110	115	128	..	105	95
3	144	140	128	..	106	101
4	101	110	104	96	104	89
1895	110	111	117	95	125	110
6	95	107	110	102	107	95
7	121	113	103	93	68	92
8	93	93	93	96	93	94
9	98	113	104	101	107	105

MEAN ANNUAL RAINFALL INDICES—*continued*

	Northern Area	East Coast	Central Area	West Coast	Canterbury	Otago-Southland
1900	111	119	108	91	101	93
1	94	94	95	103	88	101
2	97	114	82	80	119	114
3	108	95	101	88	89	96
4	126	120	113	103	120	107
1905	92	134	110	101	120	98
6	93	99	94	106	93	85
7	138	116	117	101	80	77
8	101	97	85	89	108	93
9	107	110	112	109	107	84
1910	107	108	102	106	100	72
11	96	105	107	93	124	87
12	96	102	108	100	113	105
13	85	82	103	100	101	124
14	62	82	77	92	85	99
1915	99	81	82	111	62	88
16	118	118	99	97	91	93
17	121	126	103	106	112	108
18	113	113	113	100	101	102
19	67	81	72	95	98	121
1920	112	95	123	105	100	89
21	83	77	104	110	93	95
22	93	92	87	105	82	96
23	99	114	104	91	109	102
24	123	121	121	114	101	90
1925	98	100	102	108	120	99
26	119	93	117	109	105	110
27	105	112	102	95	96	101
28	115	121	110	108	108	99
29	103	103	107	104	108	104
1930	86	88	79	77	92	84
31	91	77	96	109	85	96
32	84	98	80	83	92	92
33	95	93	86	97	85	103
34	94	79	95	89	108	99
1935	123	122	116	94	93	99
36	113	110	119	106	130	113
37	95	85	88	91	90	101
38	122	140	118	114	135	107
39	92	79	88	92	78	89
1940	93	107	94	101	104	105
41	106	111	120	104	114	102
42	95	96	100	115	101	98
43	96	111	106	92	104	90
44	111	115	107	116	124	116
1945	99	86	105	114	145	124
46	115	101	98	108	116	106
47	99	101	105	83	98	81
48	114	101	105	97	86	91
49	96	99	100	108	96	105
1950	91	115	93	90	109	88
51	102	106	106	97	127	98
52	106	114	105	94	109	89
53	109	102	123	102	116	88
54	99	105	95	96	94	92
1955	102	118	111	108	86	97
56	145	128	122	104	107	99

THE HEAT BALANCE IN SPONTANEOUS IGNITION

Part 1. THE CRITICAL STATE

By I. K. Walker, Dominion Laboratory, Department of Scientific and Industrial Research, Wellington.

(Received for publication, 17 February 1961)

Summary

A method is described for determining relationships between size and critical ambient temperatures of piles of self-heated materials, at the initial point of thermal instability, for reactions of zero order. This method is applicable whether or not the effects of temperature on reaction velocity are in accordance with the Arrhenius Law. For a single reaction, thermal instability is possible only when the reaction has a positive temperature coefficient; and it is demonstrated that if this coefficient is expressed in terms of the temperature interval necessary to change the reaction rate by a definite factor at the temperature of interest, simple equations of universal applicability can be deduced. An approximate correction can be made to allow for effects of variation of thermal conductivity with temperature. Comparisons are drawn between criteria for the critical state derived from the present equations, and the more conventional criteria. The equations are used to calculate the onset of thermal instability in spherical piles of pie wool.

Symbols and Units Employed

Δ	dimensional coordinate (3 for sphere; 2 for cylinder; 1 for slab)	
r	half-thickness of pile (radius of sphere or cylinder, half-thickness of slab)	cm
T_A	ambient temperature (defined as a perfect heat sink)	°K
T_B	surface temperature of pile	°K
T_C	central temperature in pile	°K
T_X	a selected temperature intermediate between T_C and T_A (see equation 33)	°K
Z_A	reaction rate at temperature T_A	cal sec^{-1} g^{-1}
Z_B	reaction rate at temperature T_B	cal sec^{-1} g^{-1}
Z_C	reaction rate at temperature T_C	cal sec^{-1} g^{-1}
Z_X	reaction rate at temperature T_X	cal sec^{-1} g^{-1}
t	temperature difference between central and surface temperatures	°K
t'	central temperature rise within pile in composite critical state $(= T_C - T_B)$	°K
t^*	central temperature rise within pile in critical state with surface cooled to ambient temperature $(= T_C - T_B)$	°K
t_0	central temperature rise within pile for hypothetical reaction without temperature coefficient $(= T_C - T_B)$	°K

SYMBOLS AND UNITS EMPLOYED—*continued*

θ	temperature difference between surface and ambient temperatures	°K
θ'	temperature rise at surface of pile in composite critical state ($= T_B - T_A$)	°K
θ^*	temperature rise at surface of pile in critical state, with t at a minimum ($= T_B - T_A$)	°K
θ_0	temperature rise at surface of pile for hypothetical reaction without temperature coefficient ($= T_B - T_\perp$)	°K
y	temperature interval to change reaction rate by a factor of 2	°K
A	reaction rate constant	cal sec^{-1} g^{-1}
a	initial concentration of reactant	mole cm^{-3}
$(a-x)$	reactant concentration after specific time interval	mole cm^{-3}
b	concentration "constant" after specific time interval $[= (a-x)^n]$	
n	order of reaction	
E	energy of activation	cal $mole^{-1}$
R	gas constant	cal $mole^{-1}$ $°K^{-1}$
e	Naperian base	
P	rate of total heat generation in unit section of pile bounded by r	cal sec^{-1}
P^*	rate of total heat generation in unit section of pile bounded by r, in critical state when $T_B = T_A$	cal sec^{-1}
P_0	rate of total heat generation in unit section of pile bounded by r for hypothetical reaction without temperature coefficient	cal sec^{-1}
ρ	density	g cm^{-3}
k	thermal conductivity	cal sec^{-1} cm^{-1} $°K^{-1}$
H	surface heat transfer coefficient	cal sec^{-1} cm^{-2} $°K^{-1}$
δ	dimensionless parameter (see equation 36)	
α	dimensionless parameter ($= Hr/k$)	

INTRODUCTION

"Spontaneous" ignition is so called because the material involved can ignite through reactions contained within itself, starting from temperatures around atmospheric. Although conventional combustion will occur finally, the effective "ignition temperature" is sometimes very low, by virtue of the geometry of the pile, and of the kinetics of the chemical reaction for the material involved. This "ignition temperature" is represented by a state of thermal instability in the pile of material, where self-generated heat will cause the temperature to rise indefinitely. Thermal instability of this type is often termed thermal explosion.

For convenience in mathematical treatment, piles can be considered in idealised geometrical forms such as symmetrical three dimensional piles (spheres), two dimensional (cylinders of infinite length), and one dimen-

sional (infinite plane parallel slabs). Heat can be lost from the surfaces of such piles by appropriate thermal conductivity to ambient temperature, which is here considered as a perfect heat sink. In any such pile of material undergoing exothermic reaction at a constant rate (e.g., by zero-order chemical reaction), heat is being continuously generated, and heat is being continuously lost to the surroundings. This loss of heat may be restricted entirely by conditions external to the pile, or entirely by internal conditions, or by a combination of the two. The first case (restriction by external conditions) will apply to a pile of material uniform throughout in temperature, with loss of heat from its surface to the nearest heat sink (ambient temperature) restricted by an interposed inert material, or by a surface heat transfer coefficient. The second and third cases arise when the large size of a pile and the limited thermal conductivity of its material cause the centre of the pile to become appreciably hotter than its perimeter.

If the rate of reaction is not affected by variations in temperature, the internal temperature of the pile will rise until the heat generated is equal to the heat lost. From Newton's Law of Cooling it can be seen that a pile of such material uniform throughout in temperature ($T_C = T_B$) and restricted by surface cooling only, will rise above ambient temperatures so that,

$$\theta_0 = \frac{r \rho Z_A}{\Delta H} \qquad \ldots (1)$$

A pile of material whose rate of reaction is similarly unaffected by changes in temperature, but with its surfaces perfectly cooled to ambient temperature ($T_B = T_A$) will also rise in central temperature until the heat generated is equal to the heat lost. The steady state internal temperature distribution will be symmetrical (cf. Walker and Harrison, 1960), and such that,

$$t_0 = \frac{r^2 \rho Z_A}{2 \Delta k} \qquad (2)$$

Z_A in these two equations is the reaction rate at the ambient temperature. But since this rate is here defined as independent of temperature, Z_B or Z_C could equally be substituted. A reaction of this type is incapable of causing thermal instability, since the temperature rise is always finite for finite values of the RH sides of equations (1) or (2). (However, such a reaction might conceivably cause ignition, perhaps by producing high enough values of temperature rise to cause other reactions to commence.)

If this pile of material whose reaction rate is independent of temperature is replaced by material having a positive temperature coefficient of reaction, the increased temperature of the pile will cause an increased rate of reaction, leading to further increases in temperature. The magnitude of the temperature rise will therefore depend on the temperature coefficient, as well as on the rate of reaction, the size and geometry of the pile, and the restricting thermal conductivity of the material of the pile and/or of its immediate surroundings. If the temperature coefficient is sufficiently large, the temperature rise may continue indefinitely, and a thermal explosion results. Although

reactions of order greater than zero will decrease in rate as reactant is consumed, this effect is sometimes overwhelmed in practice by changes in the dominant chemistry when large increases in temperature take place, leading to new reactions which continue the temperature rise.

If the temperature coefficient of the material (in conjunction with its reactivity) is insufficient to cause a thermal explosion, one could imagine a critical point being reached that would represent the highest central temperature rise above the surroundings consistent with a stable state. This condition is hereafter referred to as the "critical state". This critical state is of fundamental significance in spontaneous ignition for two reasons. It is important from the practical aspect since the ambient temperature then represents the "ignition temperature" of the material for the particular geometry involved. And it is important from the theoretical aspect, since this heat balance represents the state nearest to actual combustion which is easily amenable to mathematical analysis. Semenoff (1928) discussed the critical state for a gaseous reaction confined at a uniform temperature within a reaction vessel, and with all restrictions on heat flow imposed outside the reaction vessel. Frank-Kamenetskiĭ (1939) proposed a solution to the critical state for all three geometries of sphere, cylinder and slab for the case of restricted thermal conductivity within the reacting material, with the surface perfectly cooled to ambient temperature. Frank-Kamenetskiĭ's solution (1939, 1942) has been elaborated by Harris (1940), Rice (1940), and Chambré (1952). However, Carrie *et al.* (1959) have suggested a method of computing the heat balance in a sphere of reacting material, and if this is carried out for a reaction obeying the Arrhenius Law (with surface cooled to ambient temperature, and with k assumed uninfluenced by temperature) discrepancies are found between such a heat balance in the critical state and that deduced by Chambré (1952) from the tabulated functions of Chandrasekhar and Wares (1949). This computed heat balance further leads to a critical state different from that deduced by Frank-Kamenetskiĭ (1939 or 1942).

All these mathematical treatments of the critical state have been handicapped by the complexity of relationships between chemical reaction rate and temperature. The energy of activation (E) in the Arrhenius Equation is independent of temperature, and was therefore employed by the above authors to express the effect of temperature on reaction rate. Frank-Kamenetskiĭ (1939) defined the critical state in terms of a dimensionless parameter δ, and in 1942 he proposed a slightly modified expression for δ, which has been employed by subsequent workers (see equation 36). To find the value of δ, Frank-Kamenetskiĭ (1939) and following authors employed an approximation to the Binomial Theorem,

$$(1 + t^*/T_B)^{-1} \simeq 1 - t^*/T_B \qquad \ldots\ldots (3)$$

The approximation represented by (3) is inconsistent with the Arrhenius Law, and this will introduce an error of undefined magnitude into any solution of the critical state based on its use. No explanation of the physical significance of (3) has been offered by any of the authors employing it, although their solutions are stated to apply to reactions conforming to the Arrhenius Law (Frank-Kamenetskiĭ, 1939; Rice, 1940; Chambré, 1952;

Thomas, 1958). Equation (3) has the effect of rendering the Arrhenius constants A and E temperature dependent. This creates difficulties for the chemist attempting to understand the physical significance of E in Frank-Kamenetskiĭ's equation (1939, 1942) for the critical state. There are also practical difficulties in applying the equation. Although many reactions are found to obey the Arrhenius Law, such conformity is sometimes limited to restricted temperature intervals. Some spontaneous ignition reactions fail to conform to the Arrhenius Law (e.g., Burgoyne and Thomas, 1951), and constant values cannot then be found for A and E. It is thus not a simple matter to measure A and E directly in a practical experiment, since such measurement must also include an empirical demonstration that the Arrhenius Equation is applicable to the reaction in question. In view of all these facts an attempt is here made to solve the problem using a simple physical approach, and employing parameters that are easier to measure in the laboratory.

In mathematical treatment of reactions having positive temperature coefficients, the conventional form of the Arrhenius Equation is best avoided, since its constants create a temptation to apply it over wider temperature ranges than those used in the empirical determination of A and E. The Arrhenius Equation sometimes suffers deviations in practice (Semenoff, 1935), and it also makes possible changes in the dominant chemistry as the temperature changes, leading to variations in the apparent value of E (Hinshelwood, 1947). Since the Arrhenius Equation is not always obeyed over wide temperature ranges, the present treatment is based on consideration of the temperature interval (y) which changes the reaction rate by a factor of 2 at the experimental temperature T; that is, y is such that the reaction doubles between $(T - y/2)$ and $(T + y/2)$. (Any other such factor could be used, but 2 is convenient). These values of y are best determined empirically; but if the Arrhenius Equation is obeyed, it can be used to express y. It is simplest to use the classical form of the Equation, although this is known (Hirschfelder *et al.*, 1954) to be not strictly correct,

$$Z = A\,(a - x)^n \exp\,(-E/RT)$$

For a reaction of zero order (or for consideration of a specific instantaneous state in a reaction of order greater than zero) we can write,

$$Z = A\,b \quad \exp\,(-E/RT) \qquad \text{.....(4)}$$

Although (4) has been used (Chambré, 1952) in consideration of the critical state for a monomolecular reaction, b in this equation is by no means a constant for reactions of order greater than zero. Sometimes n will vary, since variations of temperature or concentration will tend to favour one order of reaction at the expense of another (Walker and Robertson, 1939). For this reason variations of temperature or of reaction mechanism can upset the constancy of b; and for reactions of order greater than zero this makes it difficult to find an equivalent point for comparison of reaction rates at different temperatures. In heterogeneous reactions, limitations of reactant diffusion rate may impose restrictions on the reaction rate, and this too may alter the

apparent order with change of temperature. Within all these limitations, for any temperature T we can write from (4),

$$y = \frac{\log 2}{\log e} (RT^2/E - Ry^2/4E)$$

The term $Ry^2/4E$ represents the asymmetry of the Arrhenius relationship in terms of y. It could be minimised by choosing a smaller factor than two for y, but presents no practical difficulty. Since $Ry^2/4E$ is very small compared with RT^2/E, we can use the obvious approximation to substitute for y^2 in this minor term. Then, to a high order of accuracy

$$y = \frac{\log 2}{\log e} RT^2/E \left(1 - 0{\cdot}12 \frac{R^2 T^2}{E^2}\right) \quad \text{.....(5)}$$

As stated above, it is always preferable to determine values of y empirically at the temperatures of interest, and this can be done with no greater experimental complication than would be needed to determine E over this same temperature interval, and without the necessity of demonstrating compliance with a specific relationship.

(1) *The Case Where* ($T_C \simeq T_B$)

Consider a pile of material uniform throughout in temperature, and with the flow of heat to the nearest heat sink restricted by a surface heat transfer coefficient (or by an interposed inert material, which can then be evaluated in terms of H). If the reaction rate is unaffected by temperature, the rise above ambient temperature will be expressed by equation (1), representing a state of stable equilibrium. If the reaction has a positive temperature coefficient represented by an invariant value of y, this temperature rise will increase the reaction rate by an initial factor $2^{\theta_0/y}$. This increase in the rate will cause a higher value of θ, leading to a fresh factor of $2^{\theta/y}$, and so on. The ratio between initial and final reaction rates is thus represented by a series; and when θ_0 is small compared to y, this series is convergent, and the pile will be in a state of stable equilibrium. For large values of θ_0/y the series becomes divergent, and stable equilibrium will no longer be possible. A thermal explosion therefore results. The critical state is produced by the highest value of the series that is still convergent; and this value is general and is not influenced by values of the individual parameters. The critical state is therefore controlled only by θ_0 and y. Since the pile is uniform in temperature, then in the critical state (cf. equation 1),

$$\theta^* = \frac{r \rho Z_C}{\Delta H} \quad \text{.....(6)}$$

If it is assumed that y is invariant over the temperature interval T_A to T_B, the infinite series culminating in $2^{\theta^*/y}$ can be evaluated by numerical integration. This shows that in the critical state,

$$\theta_0/y = 0{\cdot}5307 \quad \text{.....(7)}$$

$$Z_C/Z_A = 2{\cdot}718 \quad \text{.....(8)}$$

These same equations can be deduced from the analysis by Semenoff (1928). Now from (1), (6), (7), and (8),

$$\theta^* = 1{\cdot}443\, y \quad \text{.....(9)}$$

From (1) and (7),

$$\frac{r\ \rho\ Z_A}{Hy} = 0{\cdot}5307\ \Delta \quad \text{.....(10)}$$

For reactions having an invariant value of y, equation (10) defines the critical state for spheres, infinite cylinders, and infinite slabs of materials where temperature is practically uniform throughout the pile, and where the controlling mechanism is dominantly the self-generated temperature rise above ambient. If a thermally insulating inert material is interposed between the pile perimeter and the ultimate heat sink, H can be evaluated in terms of this thermal barrier. For similar conditions of heat flow, an identical equation can be deduced from the analysis by Thomas (1958) for a reaction stated to conform to the Arrhenius Law.

(2) *The Case Where* ($T_A \simeq T_B$)

Consider a symmetrical pile of reacting material with the surface cooled to ambient temperature ($T_B = T_A$). If the reaction has no temperature coefficient, the central temperature rise will be defined by equation (2) representing a state of stable equilibrium. If the reaction has a positive temperature coefficient, the central temperature rise will increase the central reaction rate by an initial factor $2^{t_0/y}$, thus causing an increased central rate, a higher value of t, a larger value for the factor $2^{t/y}$, and so on. As before, the ratio between initial and final central reaction rates is represented by an infinite series, which will be convergent or divergent depending on the value of t_0/y. The critical state is again produced by the highest value of the series which is still convergent; and is therefore controlled only by t_0 and y. The series cannot be evaluated in this case in a simple manner, owing to the complicated nature of the heat balance. But it is possible to solve the heat balance by other methods, and this gives the ratio of initial and final reaction rates. For each geometry this ratio yields a general solution to the sum of the series controlling the critical state.

Frank-Kamenetskiĭ (1939, 1942) considered reactions conforming to the Arrhenius Law. By making the approximation inherent in (3) he solved the heat balance for an infinite slab by mathematical analysis, and for an infinite cylinder and a sphere by numerical integration. It might be noted

that the assumption of (3) would make Frank-Kamenetskiĭ's two (1939, 1942) expressions for δ identical. Chambré (1952) used this same approximation to solve the cylindrical case analytically, and to show that the spherical case could be expressed in the same form as the equations governing an isothermal un-ionised gas sphere in gravitational equilibrium, for which the parameters have been numerically integrated and tabulated (Chandrasekhar and Wares, 1949). The use of equation (3) in this manner corresponds to the assumption of an invariant value of γ over the temperature interval T_A to T_C. Frank-Kamenetskiĭ (1939, 1942) and Chambré (1952) further assumed that k is invariant over the temperature range T_A to T_C.

The present approach to this problem is based on seeking a general solution by assuming an invariant k, and comparing the heat balance computed for a reaction with invariant E with that computed for a reaction with invariant γ. For a reaction obeying the Arrhenius Equation (i.e., invariant E) the value of γ will vary over the temperature interval T_B to T_C (equation 5). A temperature can be found for the determination of a single value of γ which leads to a computed heat balance in the critical state closely equivalent to the heat balance calculated using values of Z varying in strict accordance with the Arrhenius Equation. For each value of E there is an upper limit to the value of T_C at which such an equivalence can be found. The numerical calculations of heat balance have been carried out using the formula proposed by Carrie *et al.* (1959). By considering thin layers, the critical value of r can be recognised as the point where the value of $(r^2 \rho Z_B)$ rises to a maximum, and it is convenient to note that in the spherical case this is directly proportional to "dp" in the formula (Carrie *et al.*, 1959).

2 (A) Sphere

If $(T_B = T_A)$, and if γ and k are assumed invariant, the heat balance in the critical state has been calculated using the formula proposed by Carrie *et al.* (1959), and also by using the analysis by Chambré (1952) and the functions tabulated by Chandrasekhar and Wares (1949). Identical results were obtained by both these methods. Advantage can then be taken of equation (2) to draw comparisons between this heat balance for the critical state, and the heat balance for a hypothetical reaction without temperature coefficient, proceeding at a rate equal to the real reaction at the surface temperature. The calculation then gives ratios of central reaction rates, ratios of temperature rises, and ratios of rates of total heat production, in the two cases,

$$Z_C = 4{\cdot}99\, Z_B \qquad \text{.....(11)}$$

$$t^* = 2{\cdot}90\, t_0 \qquad \text{.....(12)}$$

$$P^* = 1{\cdot}81\, P_0 \qquad (13)$$

Evaluating P_0 in (13) in terms of Z_B,

$$P^* = 1{\cdot}81 \frac{4}{3} \pi r^3 \rho Z_B \qquad \text{.....(14)}$$

By repeating the numerical calculations (Carrie *et al.*, 1959) using values of reaction rate varying in accordance with the Arrhenius Equation, and comparing the results with those obtained using rates based on an invariant y, it is found that the best equivalence is obtained with a value of y calculated (equation 5) at a temperature of about $(T_B + 0{\cdot}85y)$. However, since the greater part of the reacting material in a sphere is located near the perimeter, and since the greater part of the temperature difference in the critical state also occurs near the perimeter, there is a simpler method of selecting the temperature at which y is to be measured in the case of a sphere, by selecting the value of y representative of the greatest bulk of the material. Consider the "average" temperature of the sphere, such that the same amount of reaction would take place if all the reactant were at this average temperature. (This can be visualised as the real reaction proceeding under conditions of perfect heat exchange at all parts of the sphere, this uniform temperature being such that the total production of heat is the same as that in the critical state). This "average" temperature we will designate as T_X, and the corresponding reaction rate will then be Z_X. Since this temperature is defined as uniform,

$$P^* = \frac{4}{3} \pi r^3 \rho Z_X \qquad \ldots\ldots(15)$$

Now as stated above, the value used for y will be one which is the best compromise over the temperature interval T_B to T_C. But no great error will arise from applying this value as an approximation over the temperature interval T_B to T_X. Then,

$$Z_X/Z_B \simeq 2^{T_X - T_B / y} \qquad \ldots\ldots(16)$$

From (14), (15), and (16), and taking logarithms,

$$T_X = T_B + 0{\cdot}854y \qquad \ldots\ldots(17)$$

This represents the temperature at which y should be measured to obtain a value which is the best compromise for use in the critical state, and for this "equivalent" value of y we can write,

$$Z_C/Z_B = 2^{t^*/y} \qquad \ldots\ldots(18)$$

From (11) and (18), and taking logarithms,

$$t^* = 2{\cdot}32y \qquad \ldots\ldots(19)$$

Then from (2), (12) and (19),

$$\frac{r^2 \rho Z_B}{ky} = 4{\cdot}79 \qquad (20)$$

This is the fundamental equation applying to the critical state in all cases of spontaneous ignition caused by zero order chemical reactions of definite kinetics (whether homogeneous or heterogeneous), assembled in the form

of spherical piles with surface cooled to ambient temperature. Values of y and k should both be determined at the temperature T_X, preferably empirically. Equation (20) applies to reactions not conforming to the Arrhenius Equation, as well as to those which do conform. If the Arrhenius Equation is obeyed, an approximation of (5) can be used to express y,

$$y = 0{\cdot}693 \frac{RT_X^2}{E} \qquad \ldots\ldots(21)$$

This involves neglect of the second term in (5), since this would cause an error of only 10^{-3} for a reaction with T_X at 640°C and with $E = 20{,}000$.

It may be more convenient to express y in terms of the known temperature T_B rather than the unknown T_X. This can be done by conventional solution for y of the obvious quadratic equation derived from (17) and (21), and then using the Binomial Theorem to expand the square root term. Thus,

$$y = 0{\cdot}693 \frac{RT_B^2}{E} + 0{\cdot}821 \frac{R^2T_B^3}{E^2} + 1{\cdot}21 \frac{R^3T_B^4}{E^3}$$

$$+ 2{\cdot}01 \frac{R^4T_B^5}{E^4} + \text{etc.} \qquad \ldots\ldots(22)$$

For reactions obeying the Arrhenius Equation, this diminishing series evaluates y in terms of T_B and E, and can be substituted directly in equation (20). However, in a practical problem where values are required for y over a range of surface temperatures, it is best to determine empirical values of y at selected values of T_X, and then plot them against a corresponding T_B (equation 17) on a graph. Or if y is to be calculated, this can be done for selected values of T_X (e.g., equation 21 or its stricter form if necessary), and corresponding values of T_B then determined from (17). Values of y (at each corresponding T_X) are again plotted against T_B on a graph.

2 (B) Cylinder

If ($T_B = T_X$), and y and k are invariant, the heat balance for the critical state can be calculated as before, and comparison made with a hypothetical reaction without temperature coefficient, proceeding at a rate equal to the real reaction at the surface temperature.

$$Z_C = 4{\cdot}00\, Z_B \qquad \ldots\ldots(23)$$

$$t^* = 2{\cdot}77\, t_0 \qquad \ldots\ldots(24)$$

$$P^* = 2{\cdot}00\, P_0 \qquad \ldots\ldots(25)$$

For this invariant value of y we can combine (18) and (23), and take logarithms,

$$t^* = 2{\cdot}00\, y \qquad (26)$$

Then from (2), (24) and (26),

$$\frac{r^2 \rho Z_B}{ky} = 2{\cdot}89 \qquad \text{.....(27)}$$

2 (C) Slab

If ($T_B = T_A$), and y and k are invariant, then as previously,

$$Z_C = 3{\cdot}27\, Z_B \qquad \text{.....(28)}$$

$$t^* = 2{\cdot}69\, t_0 \qquad \text{.....(29)}$$

$$P^* = 2{\cdot}28\, P_0 \qquad \text{.....(30)}$$

From (18) and (28),

$$t^* = 1{\cdot}71\, y \qquad \text{.....(31)}$$

From (2), (29) and (31),

$$\frac{r^2 \rho Z_B}{ky} = 1{\cdot}27 \qquad \text{.....(32)}$$

Equations (27) and (32) respectively define the critical state in a cylinder of infinite length, and in an infinite plane parallel slab, with the surfaces cooled to ambient temperature. By comparing integrations carried out with invariant y with integrations using invariant E, it is possible to find the temperature T_X at which measurement of y provides the best compromise over a wide temperature range. This is provided by a temperature such that,

$$T_X = T_A + (0{\cdot}74 + 0{\cdot}038\, \Delta)y \qquad \text{.....(33)}$$

For reactions obeying the Arrhenius Equation, values of y can be obtained in terms of T_B from equations (21) and (33). For the cylinder,

$$y = 0{\cdot}693 \frac{RT_B^2}{E} + 0{\cdot}784 \frac{R^2T_B^3}{E^2} + 1{\cdot}11 \frac{R^3T_B^4}{E^3} + 1{\cdot}76 \frac{R^4T_B^5}{E^4} + \text{etc.} \qquad \text{.....(34)}$$

And for an infinite slab,

$$y = 0{\cdot}693 \frac{RT_B^2}{E} + 0{\cdot}748 \frac{R^2T_B^3}{E^2} + 1{\cdot}01 \frac{R^3T_B^4}{E^3} + 1{\cdot}52 \frac{R^4T_B^5}{E^4} + \text{etc.} \qquad \text{.....(35)}$$

However, in a practical problem it is best to plot values of y measured empirically (or calculated) at a temperature T_X against equivalent values of T_B on a graph, as previously described.

DISCUSSION

Equation (10) defines the critical state for a pile of material uniform throughout in temperature and losing heat from its surface in accordance with Newton's Law of Cooling, which is undergoing a zero order chemical reaction having a temperature coefficient over the temperature interval of interest equivalent to an invariant value of y. If the temperature coefficient of the reaction conforms to the Arrhenius Law, this invariant state of y should be compensated by measuring y at a suitable temperature intermediate between T_A and T_C. To a first approximation, and to suit other requirements (see Part 2), the temperature T_X (equation 33) will provide this. By using equation (3) Thomas (1958) has provided a similar analysis which is equivalent to using a value of y measured at temperature T_A. There will be a small discrepancy between these two solutions, and equations (5), (9) and (33) show that for a reaction conforming to the Arrhenius Law this discrepancy will steadily increase as the ambient temperature is raised.

Consider next the critical state for a pile of material generating heat by a zero order chemical reaction, and with its surface cooled to ambient temperature. Equations (20), (27) or (32) respectively define this condition for a pile of spherical geometry, an infinite cylinder, or an infinite slab. These equations demonstrate the major role that temperature coefficient of reaction plays in the ignition mechanism. Reactions whose rate is greatly influenced by temperature (y small or E large) can cause ignition with lower values of initial reaction rate, with higher values of thermal conductivity, or with smaller-sized piles of material. The equations are in a particularly convenient form in view of the ease with which values of $\rho Z/k$ and values of y can be measured at different temperatures (Walker and Harrison, 1960). (Alternatively, if the Arrhenius Equation is obeyed, these parameters can be calculated from a knowledge of ρ, k, A, and E). Values of $\rho Z_B/ky$ can be plotted against T_B for any reaction (preferably on a log-linear scale) using for this purpose values of y and k at the corresponding temperature T_X. From this graph, critical values of r can be determined at any surface temperature.

The mathematics of spontaneous ignition represent a recognition that all ignition temperatures are affected by geometry, in the case of materials which are permeable to air and which ignite by a single oxidation reaction having a positive temperature coefficient. "Spontaneous" ignition (when caused by a single chemical mechanism) is not essentially different from other ignition, except in so far as it contravenes "commonsense" thinking. The contravention is due to the sudden nature of the change-over from stable to unstable thermal conditions which can occur when the pile is slightly raised in surface temperature. This change-over is well illustrated for the case of a sphere (with surface cooled to ambient temperature) by equations (2) and (20). Walker and Harrison (1960) demonstrated that small central temperature rises in a sphere (say up to 0·2 y) are closely

represented by equation (2), since the temperature coefficient of reaction has little effect in such a case. Equation (20) shows that if the surface of such a sphere is now raised in temperature by only 2 γ, the critical state will be exceeded, with a consequent infinite temperature rise. Equations (19), (26) and (31) show how very small is the internal temperature rise necessary (with common temperature coefficients) for a given pile of material to attain the critical state. In normal circumstances this critical state will be swiftly followed by thermal instability, and "spontaneous" ignition. Most previous discussions of the critical state (Frank-Kamenetskiĭ, 1939; Chambré, 1952; Genensky, 1957; Thomas, 1958) have been based on Todes' estimate (Todes unpublished, via Chambré, 1952) of the maximum temperature rise before thermal explosion (t^*). Equations (19) and (22) (or 19 and 21) evaluate t^* for the spherical case, and show that Todes' value is too small. Similarly (26) and (34) (or 26 and 21) evaluate t^* for the case of the cylinder, and (31) and (35) (or 31 and 21) evaluate t^* for the slab, with similar results. It may be noted that Todes' estimate would give a correct figure for the rise above ambient temperature of a pile of any symmetrical geometry in the critical state entirely under the control of surface cooling, i.e., θ^* (see equations 5 and 9).

The effects of possible variations of thermal conductivity with temperature have been ignored in previous discussions of the critical state (Frank-Kamenetskiĭ, 1939, 1942; Harris, 1940; Rice, 1940; Chambré, 1952; Enig *et al.*, 1956; Genensky, 1957; Thomas, 1958; Gross and Robertson, 1958). If values of k are known, then the variations can be allowed for by selecting a suitable "mean" value of k for use in the formula. To a first approximation the value of k measured at T_X will provide this. However, thermal conductivity measurements are not easy, and precise values for k are not always available for materials suspected of spontaneous ignition. Even without a knowledge of k or of its variations with temperature, it is possible to make some allowance for these variations in the present formulae. This can be done by using Walker and Harrison's calorimetric technique (1960) to make direct measurements of $\rho Z/k$, and substituting these values (at a temperature T_B) directly into the appropriate equation (20), (27) or (32) (depending on geometry). The effective value of k will then be at temperature T_B instead of T_X, but this can be approximately compensated by expressing γ as the empirical temperature rise necessary to double the whole factor $\rho Z/k$ instead of just Z. This modification of γ should still be measured at a temperature T_X (equation 33). This technique will slightly over-compensate for variations of k with temperature; but it is convenient to use in view of the difficulties in conventional measurement of k, and of the ease with which values of $\rho Z/k$ and of this modification of γ can be measured (Walker and Harrison, 1960).

Previous criteria for the critical state for reactions conforming to the Arrhenius Law assembled in piles with surface cooled to ambient temperature have all been based on consideration of δ. Frank-Kamenetskiĭ (1939) and Chambré (1952) both used the approximation inherent in (3) to obtain values of 3·32, 2·00, and 0·88 for sphere, cylinder, and slab respectively. Harris (1940) carried out a numerical integration for the sphere and obtained a value for δ of 3·82; and Rice (1940) similarly calculated a value of 3·3.

All these values were considered to be non-dimensional. Enig *et al.* (1956) have derived the correct differential equation governing the critical state with surface cooled to ambient temperature, but this proved so complex it had to be solved by a perturbation technique on a digital computer. Enig *et al.* (1956) obtained values of δ for the sphere ranging from 3·326 to 4·902; for the cylinder ranging from 2·002 to 2·962; and for the slab ranging from 0·880 to 1·302. They found that δ varied in this manner as the ratio T_B/E varied. In view of these conflicting values for δ it is illuminating to use the present solution to the problem to compute δ. Rewriting Frank-Kamenetskiĭ's equation (1942) in the present symbols,

$$\delta = \frac{r^2 \ \rho \ E}{k \ R \ T_B^2} A \, b \exp(-E/RT_B) \qquad \text{.....(36)}$$

This can be evaluated in terms of the present solution to the problem by substituting from (4), (20) and (22) (sphere); (4), (27) and (34) (cylinder); or (4), (32) and (35) (slab). These yield equations for δ, for a sphere,

$$\delta = 3{\cdot}32 + 3{\cdot}93\, RT_B/E + 5{\cdot}82\, \{RT_B/E\}^2 + 9{\cdot}65\, \{RT_B/E\}^3 + 17{\cdot}1\, \{RT_B/E\}^4 + 31{\cdot}9\, \{RT_B/E\}^5 + \text{etc.} \qquad \text{.....(37)}$$

For a cylinder of infinite length,

$$\delta = 2{\cdot}00 + 2{\cdot}26\, RT_B/E + 3{\cdot}20\, \{RT_B/E\}^2 + 5{\cdot}07\, \{RT_B/E\}^3 + 8{\cdot}60\, \{RT_B/E\}^4 + 15{\cdot}3\, \{RT_B/E\}^5 + \text{etc.} \qquad \text{.....(38)}$$

And for an infinite plane parallel slab,

$$\delta = 0{\cdot}88 + 0{\cdot}95\, RT_B/E + 1{\cdot}28\, \{RT_B/E\}^2 + 1{\cdot}93\, \{RT_B/E\}^3 + 3{\cdot}12\, \{RT_B/E\}^4 + 5{\cdot}29\, \{RT_B/E\}^5 + \text{etc.} \qquad \text{.....(39)}$$

Enig *et al.* (1956) considered that δ would approach a minimum value at high values of r, but equations (37), (38) and (39) show that for each geometry δ is independent of r. Table 1 shows values of δ calculated by equations (37), (38) and (39) for various values of RT_B/E. At the higher values of RT_B/E (say $> 0{\cdot}1$), the error introduced by neglecting the second term of (5) to derive (21) becomes significant. The inclusion of such corrections in (37), (38) and (39) would make them inconveniently complex, and it is easier to calculate values of δ for the larger values of RT_B/E by using the strict form of (5) in place of (21). Corrected versions of (37), (38), and (39) can thus be derived for specific values of RT_B/E. When these are used, all values of δ in Table 1 are unchanged (to the second decimal place) except those for $RT_B/E = 0{\cdot}2$, which become 4·42, 2·62, and 1·13 respectively (cf. Enig *et al.*, 1956 – 4·51, 2·68, 1·16). It is thus seen that within the limited accuracy of the present work, the calculated values of δ agree with those computed by Enig *et al.* (1956), for values of RT_B/E up

to 0·1. This value would represent a surface temperature in excess of 720°C for $E = 20{,}000$. The discrepancy at $RT_B/E = 0{\cdot}2$ is due to limitations in the present proposal to substitute an equivalent fixed value of γ for the varying values demanded by the Arrhenius Law. There is an upper limit to the value of RT_B/E above which this assumption of equivalence will introduce errors, since at high ratios of T_B/E the central temperature rise in the critical state becomes comparable to the surface temperature (°K). Above this ratio the present equations become inaccurate, but still introduce less error than solutions based on fixed values for δ.

The figures in Table 1 demonstrate that the conventional view (Frank-Kamenetskiĭ, 1939, 1942; Harris, 1940; Rice, 1940; Chambré, 1952; Thomas, 1958) that δ is independent of temperature is incorrect, and that for any given energy of activation δ asymptotically approaches a value of 3·32 (sphere), 2·00 (cylinder), and 0·88 (slab), as the absolute zero is approached. For a normal reaction obeying the Arrhenius Equation δ will

TABLE 1—Values of δ Calculated from Equations (37), (38) and (39)

RT_B/E	Sphere	Cylinder	Slab
0	3.32	2.00	0.88
0.001	3.33	2.00	0.88
0.002	3.33	2.00	0.88
0.005	3.34	2.01	0.88
0.01	3.36	2.02	0.89
0.02	3.40	2.05	0.90
0.05	3.53	2.12	0.93
0.1	3.78	2.26	0.99
0.2	4.46	2.64	1.14

have higher values, for example at room temperature for $E = 20{,}000$, values of 3·44 (sphere), 2·07 (cylinder), and 0·91 (slab). Thus if the reaction conforms to the Arrhenius Law, Chambré's solutions (1952) for δ are strictly correct only at zero values of RT_B/E. Frank-Kamenetskiĭ (1955) has stated that his equations would be correct only if the temperature rise prior to explosion were small compared with the absolute temperature of the surroundings. At first sight it might appear that this condition is best satisfied at high temperatures. However, equations (19) and (21) (or alternatively 19 and 22) demonstrate that for a sphere the temperature rise prior to thermal explosion is a function of the square of absolute temperature. A similar relationship holds for a cylinder (equations 21 and 26, or 34 and 26), and for a slab (equations 21 and 31, or 35 and 31). It can thus be seen that Frank-Kamenetskiĭ's condition (1955) is best satisfied as the absolute zero is approached. Frank-Kamenetskiĭ (1939) and Chambré (1952) employed the approximation inherent in (3), and for a reaction obeying the Arrhenius Equation this would be correct only near absolute zero. Equations (19) and (22) show that a typical reaction with spherical geometry taking place at 20°C with $E = 20{,}000$ would have $t^*/T_B = 0{\cdot}05$ (0·04 for a cylinder or slab). The discrepancies demonstrated between Frank-Kamenet-

skiĭ's equation (1942) and the present solution do not lead to large errors when Frank-Kamenetskiĭ's equation is used to calculate critical sizes of piles in most practical problems. However, without evaluation of these errors, their magnitude would not be known. Equations (20), (27) and (32) are simpler to apply than Frank-Kamenetskiĭ's equation (1942), since the parameters they require are easier to measure in the laboratory. Further, these equations are preferable to using the conception of δ, since they apply whether the Arrhenius Equation is obeyed or not. Occasionally reactions which do not obey the Arrhenius Equation show a constant value of y over a reasonably wide temperature range (e.g., Burgoyne and Thomas, 1951; Walker and Harrison, 1960) probably because of two simultaneous reaction mechanisms with one being favoured by a rise in temperature (Hinshelwood, 1947; Walker and Robertson, 1939). In such circumstances the values of δ found by Frank-Kamenetskiĭ (1939, 1942) and Chambré (1952) will be strictly correct; but it is not a simple matter to make use of this, since these authors expressed δ in terms of A and E which are no longer constants in such a case.

Many practical storage problems involve geometries such as finite cylinders, cubes, parallelepiped, etc. Frank-Kamenetskiĭ (1942) has shown the relationship between cylinders of finite and infinite length. By studying isothermal surfaces within such solids it can be seen that the simplest manner of dealing with right cylinders and cubes is by equating them to spheres of equivalent radius. In this way equation (20) can be applied directly to right cylinders by using a value 9% higher than actual for r; and to cubes by using a value 16% higher than actual for r. In a similar manner equation (27) can be applied to a square section rod of infinite length by assuming a value 9% higher than actual for r. Such treatments can be extended to other geometries.

A demonstration can be made of the application of the present equations to a practical problem by assessing the relationships between surface temperature and radius for the onset of thermal instability in spherical piles of the dry pie wool experimented with by Walker and Harrison (1960), with surface cooled to ambient temperature. Over the temperature range 45°–100°C this reaction was found to conform better to a law of invariant y than to one of invariant E. Behaviour of this type is not uncommon in spontaneous ignition mechanisms caused by reaction between oxygen and unsaturated fats (e.g., Burgoyne and Thomas, 1951). In view of the difficulties in deciding on values for the "constants" A and E for such a reaction, the present equation (20) is easier to apply to this problem than is Frank-Kamenetskiĭ's equation (1942). Walker and Harrison (1960) packed wool into their experimental flasks to a bulk density (dry) of 0·1 g cm^{-3}. This is a very loose packing by normal commercial baling standards, although quite comparable with the packing in wool bin rooms, where piles are frequently equivalent to 5 ft in radius (125 cm). Since Walker and Harrison (1960) made direct measurements of the factor $\rho Z/k$ at a range of temperatures, there is no need to use assumed values for thermal conductivity, and y can be expressed as the empirical temperature coefficient of the factor $\rho Z/k$. Substitution in equation (20) yields critical radii for

various values of the factor $\rho Z/k$ at the temperature of the surface, and these are shown in Fig. 1 converted into surface temperatures.

Any discussion of thermal instability must be limited to temperatures at which experimental measurements of reaction kinetics have been made, since there are dangers in attempting to extrapolate the data to other temperatures. In addition, there are several sources of error in the present discussion caused by simplifying assumptions. The wool in these experiments (Walker and Harrison, 1960) was dry, and therefore showed (Walker and Harrison, 1961) a higher rate of reaction than might be expected under conditions of normal commercial regain. Although normal regain (i.e., equilibrium moisture content) has little effect on thermal conductivity at the same bulk density, if the equilibrated wool occupies the same volume the increased

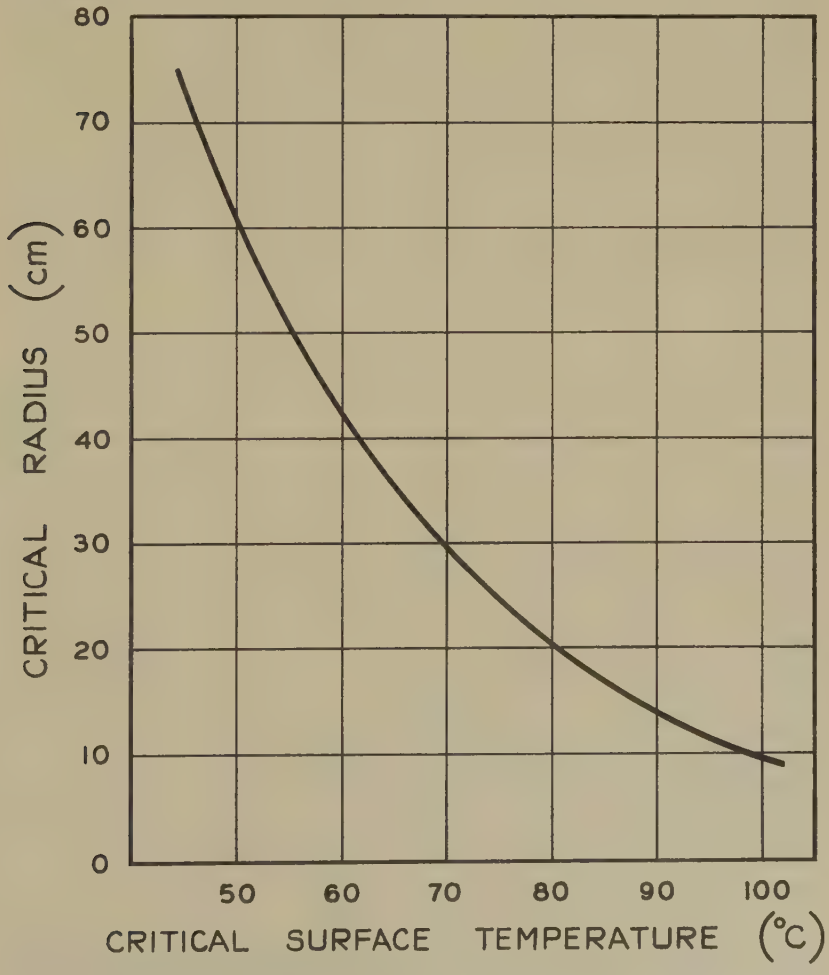

FIG. 1—Application of Equation (20) to pie wool (ref. Walker and Harrison, 1960).

density will increase the thermal conductivity (WIRA, 1955). Both these effects would make piles more stable under commercial conditions than here calculated. However, the greatest source of error lies in the assumption of zero order of reaction. Although some attention has been paid to the effects of reactant loss in gas phase reactions, most investigators of spontaneous ignition mechanisms have either ignored the significance of order of reaction with respect to solid (or liquid) reactant, or have assumed it to be zero. The position has been further confused by mathematical approaches which discuss first order (monomolecular) reactions, but use a form of the Arrhenius Equation applicable only to a zero order reaction (Enig *et al.*, 1956; Genensky, 1957; Gross and Robertson, 1958); or ignore the implications of the Arrhenius Equation (Chambré, 1952). The significance of a reaction order greater than zero with respect to solid reactant is that the reaction rate will decrease with time, and this decrease will occur to a greater extent in hotter portions of the pile than in the cooler portions. Since the present pie wool reaction has an order greater than zero with respect to solid reactant (Walker and Harrison, 1960), these calculations of thermal instability based on experimental readings at an early stage of the reaction (Walker and Harrison, 1960) represent a maximum hazard, since reactant will be used up in raising the wool from room temperature to the critical temperature. Any predictions of the surface temperature that will be necessary to support the critical state in a given pile, would therefore need to be steadily raised as the pile temperature rises above ambient.

CONCLUSIONS

1. Whether or not the effect of temperature on reaction rate conforms to the Arrhenius Law, a simple equation can be deduced governing the critical state of a spherical pile with surface cooled to ambient temperature (Equation 20). Similar equations govern the cases of semi-infinite cylinders and slabs (27 and 32). These equations are simpler and more accurate than Frank-Kamenetskiĭ's equation.

2. Frank Kamenetskiĭ's dimensionless parameter δ is temperature dependent; and at normal atmospheric temperatures and above it has values in excess of the generally accepted 3·32 (sphere), 2·00 (cylinder), and 0·88 (slab).

3. The present solution to this problem is limited to reactions of zero order; or to reactions of order greater than zero, but considered in an instantaneous state at a specific stage in the reaction. This restriction would also apply to previous solutions to the problem.

4. Application of the present equations to published data defines the limiting conditions for the onset of thermal instability in spherical piles of a specific sample of pie wool.

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Part 2. THE EFFECTS OF SUPERIMPOSED NEWTONIAN SURFACE COOLING

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Summary

The method described in Part 1 for determination of relationships between size and critical ambient temperatures of symmetrical piles of self-heated materials at the initial point of thermal instability, is extended to cover the composite case where thermal instability is due partly to temperature rise within the pile and partly to a rise of the surface temperature above ambient. This method is applicable whether or not the effects of temperature on reaction velocity are in accordance with the Arrhenius Law. The derived equations are limited to reactions of zero order. Comparisons are drawn between criteria for the critical state derived from the present equations, and the more conventional criteria. The use of the equations is demonstrated in calculations of critical ambient temperatures for spherical piles of pie wool.

INTRODUCTION

Spontaneous ignition can be caused by a pile of reacting material attaining a state of thermal instability, where the temperature will rise indefinitely. This state of thermal instability is possible only for a reaction having a positive temperature coefficient, and can be caused by restrictions to heat flow imposed by conditions external to the pile, with the interior at a uniform temperature ($T_B = T_C$) (Semenoff, 1928); or by restrictions to heat flow imposed by conditions internal to the pile, with the surface at ambient temperature ($T_B = T_A$) (Frank-Kamenetskiĭ, 1939, 1942; Chambré, 1952).

It is possible for a third type of thermal instability to occur, through a combination of restrictions on heat flow imposed externally to the pile, together with internal restrictions. In such a case the surface of a perfectly symmetrical pile will assume a uniform temperature intermediate between T_A and T_C. Genensky (1957) developed an analytical solution to the critical state for a spherical pile in this composite case with Newtonian surface cooling. And for this same composite case Thomas (1958) developed solutions to the critical state for spheres, for cylinders of infinite length, and for infinite plane parallel slabs, by an extension of the analysis by Chambré (1952). Both these analyses involve considerable mathematical complication, and both present solutions in graphical form to facilitate computing. Although the analysis by Thomas (1958) is specifically stated to apply to reactions conforming to the Arrhenius Law, mathematical approximations are employed which render the equations temperature-dependent (Walker, Part 1). Further, if an attempt is made to apply either of the above analyses to reactions not conforming to the Arrhenius Law, difficulties will arise in evaluating the "constants" A and E.

For zero-order reactions both conforming or not conforming to the Arrhenius Law, Walker (Part 1) proposed solutions to the critical state with temperature uniform within the pile ($T_C = T_B$), and to the critical state

with surface cooled to ambient temperature ($T_B = T_A$). The present work extends this treatment to cover the composite critical state where $T_C \neq T_B \neq T_A$. In this composite critical state controlled by a combination of t and θ we can speak of control by $(t' + \theta')$.

1. *The Case Where* $(t' > > \theta')$

In the critical state under dominant control of t^* where the surface is effectively cooled to the nearest heat sink, the flow of heat from the surface will still create a small temperature difference, proportional to the heat flow, and inversely proportional to the thermal conductivity of the surrounding medium. Or if the surface of the pile is freely exposed to the atmosphere, a small temperature difference will occur between surface and ambient atmosphere, proportional to the heat flow and inversely proportional to the surface heat transfer coefficient. When θ' is thus negligibly small in comparison with t^*, it can be designated $\theta_{(\min)}$. In the case of a sphere, from Newton's Law of Cooling,

$$\theta_{(\min)} = \frac{P^*}{4 \pi r^2 H} \qquad \text{.....(40)}$$

By expressing P_0 in terms of Z_B for each pile geometry, and substituting in an expression in the form (40) together with (13) and (20) (for the sphere), (25) and (27) (for the cylinder), and (30) and (32) (for the slab), we find that for each geometry,

$$\theta_{(\min)} = 2{\cdot}89\ ky/Hr \qquad \text{.....(41)}$$

Since k, y, and H may all vary with temperature, evaluation of $\theta_{(\min)}$ is most easily made by plotting values of ky/H at a range of temperatures, and substituting for r. If the temperature scale of the graph is taken as T_B then values of k and y should be chosen in each case at a corresponding T_X (equation 33) for the reaction under consideration.

(2) *The Universal Case* $(T_A \neq T_B \neq T_C)$

Equation (41) is valid only when θ' is small compared to t', say not more than 5%. A solution can also be found applicable to all cases intermediate between (10) and (20) (for a sphere); between (10) and (27) (for a cylinder); and between (10) and (32) (for a slab). This can be done by considering values for θ' and t' in the two extreme cases. Consider first the critical state under control of external temperature difference only $(T_C \simeq T_B)$. Equations (6) and (8) then yield the value of θ^* for the three geometries,

$$\theta^* = \frac{2{\cdot}72}{\Delta} \frac{r\ \rho\ Z_A}{H} \qquad (42)$$

Up to this point we have considered t' as negligible for this reaction under the dominant control of θ^* (i.e. $k/H \rightarrow \infty$). However, although very

small, t' is not zero and can be designated $t_{(min)}$. From (2) and (8) the value of $t_{(min)}$ corresponding to θ^* is (for all three geometries),

$$t_{(min)} = \frac{1{\cdot}36}{\Delta} \frac{r^2 \rho Z_A}{k} \qquad \text{.....(43)}$$

2 (A) *Sphere*

Consider the critical state under control of internal temperature difference only ($T_A \simeq T_B$). Then equations (2) and (12) yield,

$$t^* = 0{\cdot}484 \frac{r^2 \rho Z_A}{k} \qquad \text{.....(44)}$$

As defined in (40), θ' may be considered as exerting a negligible influence in the case of this reaction under the dominant control of t^* (i.e., $H/k \to \infty$). However, $\theta_{(min)}$ is not zero. From (14) and (40) the value of $\theta_{(min)}$ corresponding to t^* is,

$$\theta_{(min)} = 0{\cdot}602 \frac{r \rho Z_A}{H} \qquad \text{.....(45)}$$

The composite critical state governed by a combination of both internal and external temperature differences is under control of $(t' + \theta')$. In this case equations (42) to (45) set limits for the ratio t'/θ'

ranging from $0{\cdot}803\, Hr/k$ (under control of t^*)

to $0{\cdot}500\, Hr/k$ (under control of θ^*)

At these two extremes the numerical factor in this expression is relatively unimportant, since Hr/k then itself exerts a controlling influence on the ratio. However, in the intermediate case controlled by $(t' + \theta')$ an intermediate numerical factor can be used as a compromise; and the error this will introduce at the two extreme cases (i.e., control by t^* or control by θ^*) will be of negligible importance in the criterion for the critical state. Because of the greater influence of θ' (equation 9) we can choose as an approximation a numerical factor of 0·7, and write,

$$t'/\theta' \simeq 0{\cdot}7\, Hr/k \qquad \text{.....(46)}$$

Next consider the relationships between t', θ' and y. The actual relationships are complicated, but equations (9) and (19) set limits to the composite temperature rise $(T_C - T_A)$ before thermal instability occurs, and this composite temperature rise must lie somewhere between these limits in all cases of control by a combination of $(t' + \theta')$. To simplify the mathematics, we can assume as an approximation a relationship,

$$y \simeq \frac{t'}{2{\cdot}32} + \frac{\theta'}{1{\cdot}443} \qquad \text{.....(47)}$$

From (46) and (47),

$$t' + \theta' = \frac{y}{0{\cdot}990\ k/Hr + 0{\cdot}431} + \frac{y}{0{\cdot}302\ Hr/k + 0{\cdot}693} \quad \ldots\ldots(48)$$

Equations (43) and (44) show that in the two extreme cases there is no great variation in the numerical factor for t'. Since $t_{(\min)}$ is of negligible importance in the criterion for the composite critical state, we can adopt (44) as the approximate value for t'. On a similar argument we can adopt (42) as the approximate value for θ'. Then substituting these values for t' and θ' in (48), and rearranging,

$$\frac{\rho Z_A}{y} = \frac{\dfrac{1}{0{\cdot}990\ k/Hr + 0{\cdot}431} + \dfrac{1}{0{\cdot}302\ Hr/k + 0{\cdot}693}}{0{\cdot}484\ r^2/k + 0{\cdot}906\ r/H} \quad \ldots\ldots(49)$$

2 (B) Cylinder

A similar treatment shows,

$$t^* = 0{\cdot}693\ \frac{r^2\ \rho\ Z_A}{k} \quad \ldots\ldots(50)$$

$$\theta_{(\min)} = 1{\cdot}00\ \frac{r\ \rho\ Z_A}{H} \quad \ldots\ldots(51)$$

t'/θ' ranging from $0{\cdot}693\ Hr/k$ (under control of t^*)
to $0{\cdot}500\ Hr/k$ (under control of θ^*)

$$t'/\theta' \simeq 0{\cdot}6\ Hr/k \quad \ldots\ldots(52)$$

$$y \simeq \frac{t'}{2{\cdot}00} + \frac{\theta'}{1{\cdot}443} \quad \ldots\ldots(53)$$

$$\frac{\rho Z_A}{y} = \frac{\dfrac{1}{1{\cdot}16\ k/Hr + 0.500} + \dfrac{1}{0{\cdot}300\ Hr/k + 0{\cdot}693}}{0{\cdot}693\ r^2/k + 1{\cdot}36\ r/H} \quad \ldots\ldots(54)$$

2 (C) Slab

A similar treatment shows,

$$t^* = 1{\cdot}35 \frac{r^2 \rho Z_A}{k} \qquad \text{.....(55)}$$

$$\theta_{(\min)} = 2{\cdot}28 \frac{r \rho Z_A}{H} \qquad \text{.....(56)}$$

t'/θ' ranging from $0{\cdot}592\, Hr/k$ (under control of t^*)

to $0{\cdot}500\, Hr/k$ (under control of θ^*)

$$t'/\theta' \simeq 0{\cdot}55\, Hr/k \qquad \text{.....(57)}$$

$$y \simeq \frac{t'}{1{\cdot}71} + \frac{\theta'}{1.443} \qquad \text{.....(58)}$$

$$\frac{\rho Z_A}{y} = \frac{\dfrac{1}{1{\cdot}26\, k/Hr + 0{\cdot}585} + \dfrac{1}{0{\cdot}322\, Hr/k + 0{\cdot}693}}{1{\cdot}35\, r^2/k + 2{\cdot}72\, r/H} \qquad \text{.....(59)}$$

DISCUSSION

Equation (41) defines the effect of Newtonian surface cooling on a symmetrical pile of material undergoing zero order reaction in the critical state dominantly under the control of internal temperature rise. It will apply only whilst θ' is so small compared to t' that it has a negligibly small effect on the stability of the critical state. Gross and Robertson (1958) proposed a method of calculating θ' for the spherical case based on a similar assumption that it would have a negligibly small effect on thermal instability, but failed to specify that θ' be restricted to a small fraction of t' in these circumstances. This causes a reverse curvature at high temperatures, when a plot is made of the relationship between pile radius and self-ignition temperatures calculated by their formula (Gross and Robertson, 1958).

Equations (49), (54) and (59) respectively define the critical state for spheres, cylinders, and slabs, for the composite case under control of a combination of both internal and external temperature differences, for piles of materials undergoing zero order reaction. In all three equations a value of y should be used corresponding to a temperature T_X (equation 33). Because of approximations made in deriving (49), (54), and (59), they are not quite as accurate as (20), (27) and (32), or as accurate as (10),

which respectively define the critical state in reactions wholly under the control of internal temperature difference, or wholly under control of external temperature difference. Examination of (49), (54) and (59) shows that in the extreme case of $H/k \to \infty$ they reduce to (20), (27) and (32) respectively. Similarly, in the extreme case of $k/H \to \infty$ they all reduce to equation (10). It will be noticed that by multiplying both sides of (49), (54) and (59) by r^2/k they can be obtained in terms of α (cf. Thomas, 1958).

In comparison with previous solutions to this problem (Genensky, 1957; Thomas, 1958), equations (49), (54) and (59) offer the advantage of simplicity in computing, without the need to convert values on a graph, and without the conception of δ which needs fresh evaluation for every value of RT_B/E. They also avoid the need for evaluation of the Arrhenius constants A and E together with experimental demonstration that the reaction involved conforms to the Arrhenius Law, substituting instead experimental measurement of Z and γ at the temperatures of interest. Since Thomas (1958) based his treatment on Chambré's analysis (1952), it is strictly correct (for any given E) only at temperatures approaching absolute zero. Thomas (1958) expresses his results in the form of a graph of δ against α ($\alpha = Hr/k$). By using (4) in combination with (49), (54) and (59), a comparison can be made between the present solution and that of Thomas (1958) at temperatures approaching absolute zero. Agreement is complete for the two extremes of ($\alpha \to 0$) and ($\alpha \to \infty$), and all other values for δ fall a little below Thomas' values. The greatest discrepancies occur at about $\alpha = 4$, and are 0·19 for a sphere, 0·08 for a cylinder, and 0·02 for a slab. This closer agreement for a slab might be expected from a comparison between equation (9) and equations (19), (26) and (31). The discrepancies between the present treatment and that of Thomas (1958) are due to approximations in the derivation of the present equations (49), (54) and (59). However, the above comparisons are applicable only at temperatures approaching absolute zero. At room temperature and above, the true values of δ will be higher than the values assumed by Thomas for high values of α Walker (Part 1). And at low values of α the measurement of γ at T_γ (equation 33) will further raise values of δ. It is thus seen that despite the approximations in (49), (54) and (59) they are as accurate as Thomas' treatment for normal values of activation energy, at atmospheric temperatures and above, for zero order reactions obeying the Arrhenius Law.

Although accurate calculation of this composite critical state may be possible if the reacting sphere is separated from the nearest heat sink (T_A) by an inert thermally insulating medium, no great accuracy can be achieved if the temperature difference between surface and ambient is due to a surface heat transfer coefficient. There are three reasons for this. First there is doubt over the value to be allotted to the surface heat transfer coefficient, and over its variations both with temperature and with the convection currents which a large value of θ is bound to cause. Next there is a possible physical limitation to equations (49), (54) and (59) not immediately obvious from the mathematics. If θ' is comparable in magnitude with t' the symmetry of internal temperature distribution may become disturbed; and it is on the maintenance of this symmetry that the accuracy of the whole argument depends.

The third reason is that in small spheres of porous materials (where surface cooling might play a major role in the instability mechanism) the free convection of air through the mass will remove a great deal of heat. Little attention has yet been given to this problem of internal convection in porous materials, although its importance was recognised for large unidimensional piles (i.e., infinite slabs) by Burgoyne and Thomas (1951). Small spherical piles require a more vigorous reaction rate to develop thermal instability than do large piles (of the same materials), and therefore require a correspondingly greater supply of air if the reaction is to be maintained. Thus at radii and reaction rates where Newtonian cooling becomes important, internal convection is likely to be a significant factor in keeping the reaction maintained. Moreover, in the critical state, the temperature rise in these small spheres is much the same as that in larger spheres, and the temperature gradient is therefore steeper, leading to more vigorous internal thermal convection. Expressed another way, the effective cooling surface of a small sphere of porous material is larger than the simple spherical surface. These three difficulties will handicap any mathematical treatment of a spherical pile in the critical state midway between control by internal temperature difference and control by external temperature difference, when the surface heat losses are dominantly due to surface heat transfer coefficient to an ambient atmosphere.

The present treatment is limited to reactions of zero order, or reactions of order greater than zero but considered in an instantaneous state at a specific stage of the reaction. Genensky (1957) proposed an analytical solution for a spherical pile generating heat according to a first-order unimolecular reaction law. However, a study of Genensky's mathematics (1957) shows that the form of the Arrhenius Equation which he employed is applicable only to a zero order reaction. This restriction to zero order reactions therefore applies to all existing solutions to this problem.

Walker (Part 1) calculated critical surface temperatures for spheres of the dry pie wool investigated by Walker and Harrison (1960), with surface cooled to ambient temperature. The application of the present equation (49) can be demonstrated in calculating critical ambient temperatures for spheres of the same wool, assuming that heat transfer to ambient is not perfect, but is limited to 5×10^{-4} cal sec^{-1} cm^{-2} $^{0}C^{-1}$, a common value of surface heat transfer coefficient. By multiplying both sides of (49) by r^2/k it can be obtained in terms of $\rho Z/k$, γ and α. Since α has only a small effect, no appreciable error is introduced by using computed values of k (Walker and Harrison, 1960) to obtain α. An approximate correction for the variation of k with temperature can be made by employing for γ the temperature coefficient of the whole factor $\rho Z/k$. Walker and Harrison (1960) quote values for $\rho Z/k$ and for this modification of γ between 45° and 100°C, and substitution of these values in (49) enables calculation of critical ambient temperatures at each radius. If the critical ambient temperatures obtained in this way are plotted in Fig. 1 of Part 1 (p. 325) they would be almost indistinguishable from the critical surface temperatures, since they are removed little more than the line width from the original figures. The greatest deviations occur at high temperatures; and at a surface temperature of 100°C the critical ambient temperature for 9·7 cm radius is 99·5°C. This

demonstrates how small a part is played by surface cooling in common spontaneous ignition mechanisms in commerce. As mentioned above, in the case of this small sphere of wool (9·7 cm radius), internal convection might well play a greater role in removing heat than would Newtonian cooling.

Carrie *et al.* (1959) examined this same pie wool at an earlier date, and consequently a somewhat higher reactivity (Walker and Harrison, 1960, 1961). They packed the dry wool to a bulk density of 0·363 g cm^{-3}, typical of the density (dry) in a tight pressed ("dumped") bale of New Zealand wool. By assuming a value for k of $1{\cdot}147 \times 10^{-4}$, they deduced that at 60°C the wool was reacting with dry air to produce $25{\cdot}1 \times 10^{-6}$ cal sec^{-1} g^{-1}. If it be assumed that the temperature coefficient of reaction measured at the later date (Walker and Harrison, 1960) would apply to this same wool at the earlier date (Carrie *et al.*, 1959), the minimum ambient temperature for the onset of thermal instability in a spherical (44 cm radius) bale of the pie wool employed by Carrie *et al.* (1959) can be calculated. It is known that the surface temperature of such a bale in the critical state would rise very little above ambient temperature (Carrie *et al.*, 1959; Walker and Harrison, 1960), so it is quite accurate (and more convenient) to use (20) and (41) to calculate the critical surface and ambient temperatures. Substitution in (20) of Walker and Harrison's measured value for y and computed values for k, and of Carrie *et al.*'s values (1959) for r and ρ, shows that the critical magnitude of Z_B would be $7{\cdot}1 \times 10^{-6}$ cal sec^{-1} g^{-1}, corresponding to a surface temperature of 43·2°C. Under these conditions (41) shows that if a surface heat transfer coefficient of 5×10^{-4} cal sec^{-1} cm^{-2} $°C^{-1}$ is assumed, Newtonian surface cooling would create a temperature difference of only 0·1°C between the surface of the bale and a stable ambient temperature of say 43·1°C. This confirms the conclusion drawn by Carrie *et al.* (1959) that this spherical bale of pie wool could not cause spontaneous ignition in ambient atmospheres up to 40°C. The conclusion is strengthened by the fact that this large bale would be more restricted in its reaction by ventilation conditions than was the experimental vessel used to obtain the data on which the calculation is based, making the 44 cm bale more stable than here calculated. Further confirmation of the conclusion is afforded by the fact that this particular pie wool fired in Walker and Williamson's test (1957) in 66 minutes, whereas three other pie wools known to have caused fires in commerce (Walker and Williamson, 1957) fired in this test in 15, 21, and 37 minutes respectively.

ACKNOWLEDGMENTS

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OBSERVATIONS ON SEX DIFFERENTIATION AND CYTOTAXONOMY OF THE NEW ZEALAND SPECIES OF THE HYMENANTHERINAE (VIOLACEAE)

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Summary

Melicytus and *Hymenanthera* cannot be sharply separated, as, firstly, the species form a graded series characterised by a progressive reduction and fusion of floral parts, and, secondly, an intergeneric hybrid has a regular meiosis and normal pollen.

In hermaphrodite and unisexual flowers, a female phase follows a male phase of development. In females, the anthers collapse at a definable stage which is associated with the rate, or stage, of ovular development. In males, ovular development is inhibited soon after its inception.

Introduction

The 13 species of the sub-tribe Hymenantherinae (Rinoreeae: Violaceae) have been divided into two genera, *Melicytus* and *Hymenanthera.* Their centre of diversity is New Zealand, where the 10 representatives form a polyploid series on the basis of x = 16 (Beuzenberg and Hair, 1959; and Table 1). The species found elsewhere are *Melicytus fasciger, Hymenanthera latifolia,* and *H. dentata.*

According to Bentham and Hooker (1862), Melchior (1925), and Cheeseman (1925), *Melicytus* differs primarily from *Hymenanthera* in two respects: it has free rather than coherent anthers (except in *M. lanceolatus*), and it has several rather than one ovule per carpel. *Melicytus,* further, is entirely dioecious so far as is known, whereas *Hymenanthera* contains both dioecious and hermaphrodite species. It should be noted that dioecy is an exceptional condition in the Violaceae.

The present paper is devoted to observations on sexual differentiation in the group, and to studies which suggest that the two genera are not clearly separable.

Methods

Mitosis was examined in Feulgen squashes of root tips or leaf buds. For diploid and tetraploid species, pretreatment in colchicine and fixation in Carnoy was adequate, but the scoring of higher numbers was facilitated by using oxyquinoline and lactic alcohol after the method of Jacobsen (1954). For studies on meiosis, anthers were fixed in aceto-carmine as modified by Thomas (1940) and squashed in iron aceto-carmine. For developmental studies in male, female, and hermaphrodite plants, flower buds were fixed in 2BE or in Carnoy-Craf, sectioned at 12–20 μ, and stained in crystal violet or in Feulgen, with or without fast green as counterstain.

Voucher herbarium specimens of the species mentioned in Table 1 have been housed at the Botany Division, Department of Scientific and Industrial Research.

OBSERVATIONS

Sex Expression

As reported by Cheeseman (1925), *Melicytus, Hymenanthera chathamica* and *H. novae-zelandiae,* are confirmed as being dioecious, but *H. obovata* has been found in this study to be hermaphrodite, not dioecious as reported by Cheeseman. *H. alpina* and *H. crassifolia* are also hermaphrodite; *H. angustifolia* has a diploid race which is dioecious and a tetraploid race which is hermaphrodite.

Sex Differentiation

At an early stage of floral development, androecial and gynoecial primordia are both produced, and hence initially all species are potentially hermaphrodite. The male and female phases are successive, the differentiation of sporogenous tissue of the anther being well in advance of the initiation of ovular protuberances from the placentae.

In dioecious species further development of the ovules in males and of the microsporangia in females is arrested. At maturity in both sexes the rudiments of the opposite sex are invariably visible (Fig. 1).

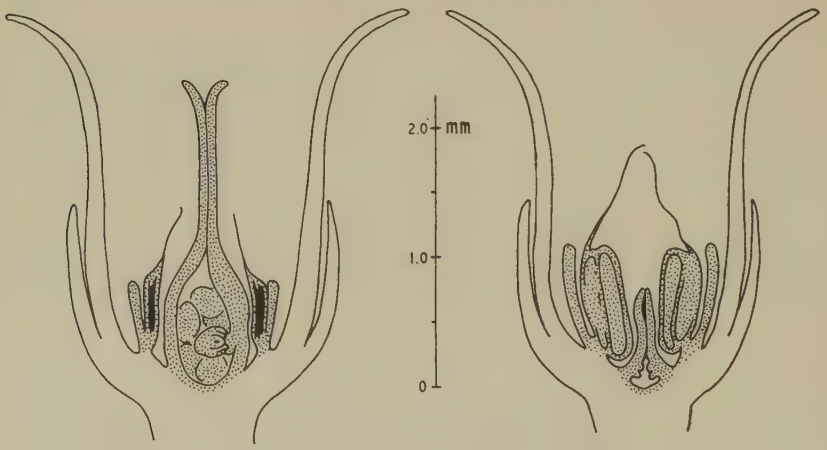


FIG. 1—Mature female and male flowers compared in *Melicytus lanceolatus.*

FEMALE FLOWERS

Long before the ultimate collapse of the anthers, the middle layers of the anther wall and the tapetum already show signs of abnormal behaviour. Thus, there is no compression of the middle layers as seen in males and

hermaphrodites of comparable age. Such a difference is already apparent by the time the tapetum is delimited. Further, the first obvious sign of arrested tapetal development is vacuolisation, which occurs some time before the general disintegration of the tapetum. In hermaphrodites and males, on the other hand, the tapetum remains rich in dense cytoplasm and persists until the wall thickenings of the endothecium appear.

Breakdown of the vacuolised tapetum may or may not precede collapse of the pollen mother-cells or young pollen (compare Figs 2, 3, 5, and 9). In either event, the tapetal cells become detached from the anther wall and break up into irregular units minus cell contents. In the meantime, the pollen mother-cells become irregular in shape, plasmolyse, and cohere in groups when squashed. Meiosis apparently continues until chromosome movement is checked by the shrinking cytoplasm; the chromosomes then become diffuse (Fig. 20) and finally coagulate into an amorphous mass. The cell contents disappear rapidly, leaving a network of almost empty cell walls. The final stage in degeneration is the swelling, separation, and collapse of the middle layers and of the endothecium; the flattened loculi are now empty of all but an irregular strand of compressed cell walls. No changes in the epidermal cells were observed.

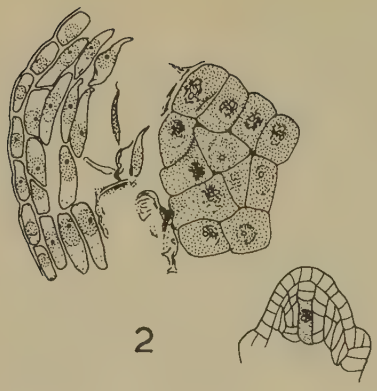
The time of collapse of the pollen mother-cells can be defined in each species (Table 1) and appears to regress as the season advances. Thus, early in the season, male abortion occurs after first metaphase or anaphase in *Melicytus macrophyllus* but in young pollen in *M. lanceolatus;* later in the season, degeneration is earlier, namely at prophase in the former species, but in tetrads in the latter.

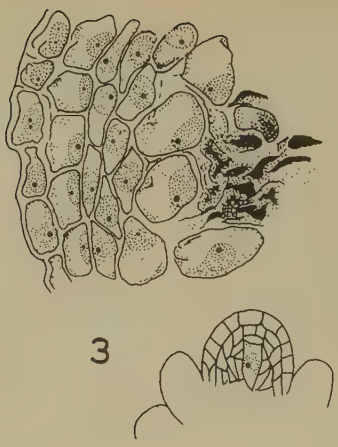
The timing relationships of male and female development are depicted and compared in Figs 2–13. In female plants, differentiation of the megaspore mother-cell coincides in time with collapse of the pollen mother-cells; in hermaphrodite species, this differentiation occurs after the formation of tetrads (Fig. 14).

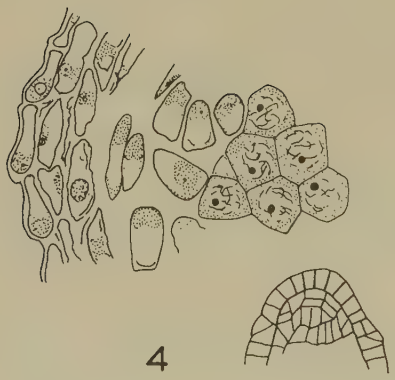
Male Flowers

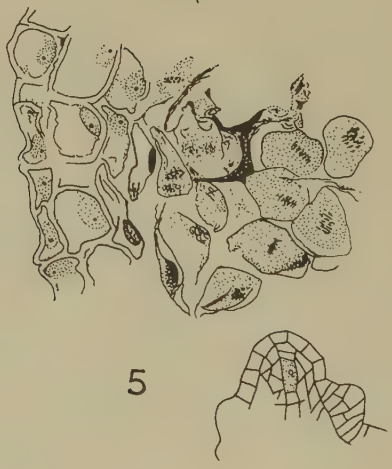
Male flowers, like the females, exhibit a rudimentary bisexuality. But whereas the anthers in the female flowers have invariably reached an advanced degree of development before collapse, the differentiation of female organs in the male flowers is arrested at an early stage: a gynoecium is produced but remains small and non-functional (Fig. 1). Rounded ovular protuberances are initiated, but archesporial tissue and integuments are not formed, except under special conditions. One such exception was found late in the season in a plant of *Hymenanthera chathamica* which was growing in dense shade. In this instance both integuments and embryo-sacs developed at first but aborted as the flower matured (Fig. 17). In the only available plant of *Melicytus micranthus* var. *microphyllus*, which was a male with tetramerous flowers, female development progressed a little further than in var. *micranthus*, which is normally pentamerous.

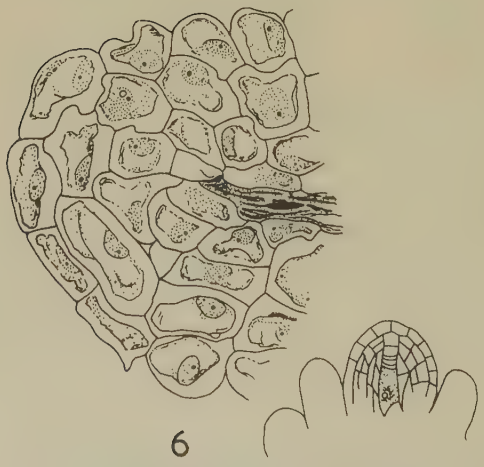
Degeneration of female tissue sometimes occurs just before anthesis and may then be observed at the apex of the nucellus (Figs 15 and 16), and more rarely in the lining of the stylar canal.

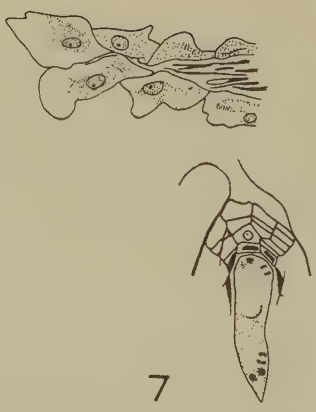








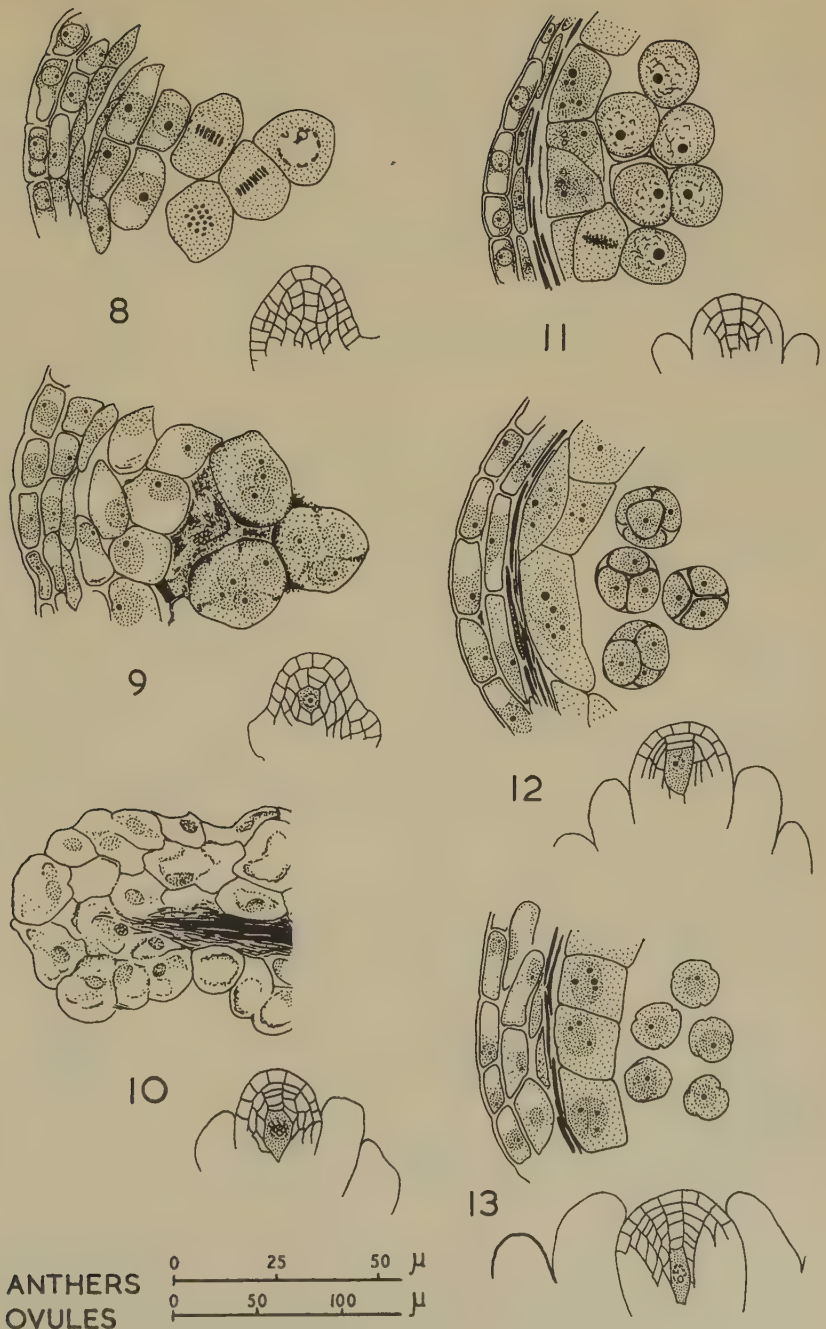




FIGS 2 to 13—Timing relationships of male and female development in the same flowers.

Prophase degeneration: FIG. 2—*Melicytus ramiflorus*;

Metaphase degeneration: FIG. 3—*M. macrophyllus* × *M. lanceolatus*; FIGS 4–7—*M. macrophyllus*.



Tetrad degeneration:
Normal development (Hermaphrodites):

FIGS 8–10—*M. lanceolatus*;
FIGS 11, 12—*Hymenanthera alpina*;
FIG. 13—*H. obovata.*

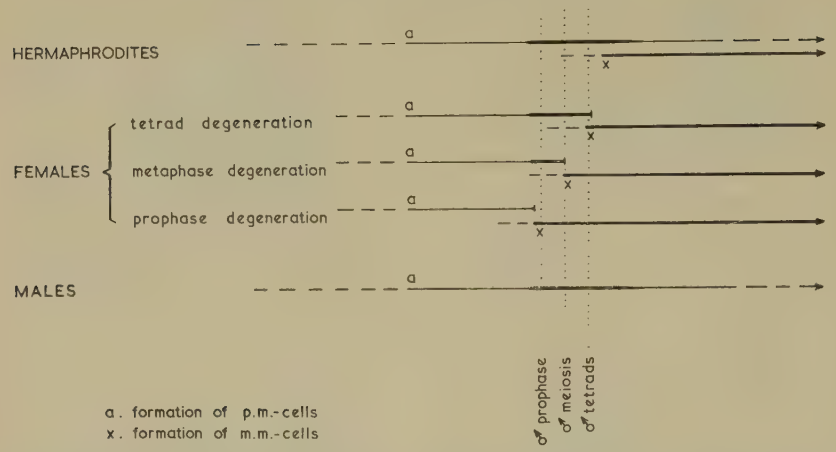


FIG. 14—See text. [NOTE—Whether female plants as compared with hermaphrodites have a retarded male phase or an accelerated female phase cannot be ascertained.]

Flower Structure

The young anthers of all species are rounded and free, but in most species subsequent marginal growth in the dorsal lobes and apical prolongation of the connectives result in a greater or lesser amount of fusion, by interlocking of the opposed epidermal cells. Fig. 18 shows the series traced.

The condition in the hybrid *Melicytus lanceolatus* × *Hymenanthera chathamica* is intermediate between the two parents, whereas in the hybrid *Melicytus macrophyllus* × *M. lanceolatus* the anthers are free, as in the maternal parent.

The modal numbers of carpels per ovary and ovules per carpel are recorded in Table 1. There is also a wide variation about these values, both within and between individuals of the same species (Fig. 19), and the

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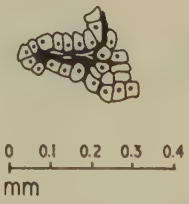

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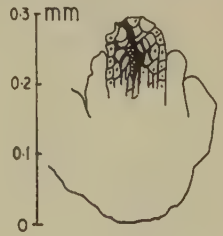

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FIGS 15, 16, 17—Three stages in ovule degeneration in
Hymenanthera novae-zelandiae (Fig. 15).
Melicytus lanceolatus × *Hymenanthera chathamica* (Fig. 16).
Hymenanthera chathamica (Fig. 17).

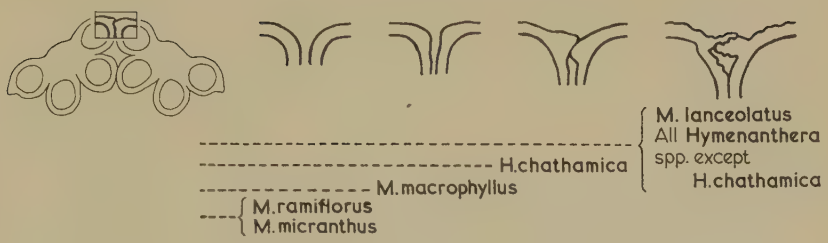

FIG. 18—See text. The portion within the square is shown magnified in the developmental stages on the right.

overall picture suggests that the species, and the genera, are more or less intimately connected by several overlapping series of reductions and fusions. No consistent differences were found in ovule and carpel numbers between male and female flowers of the same species.

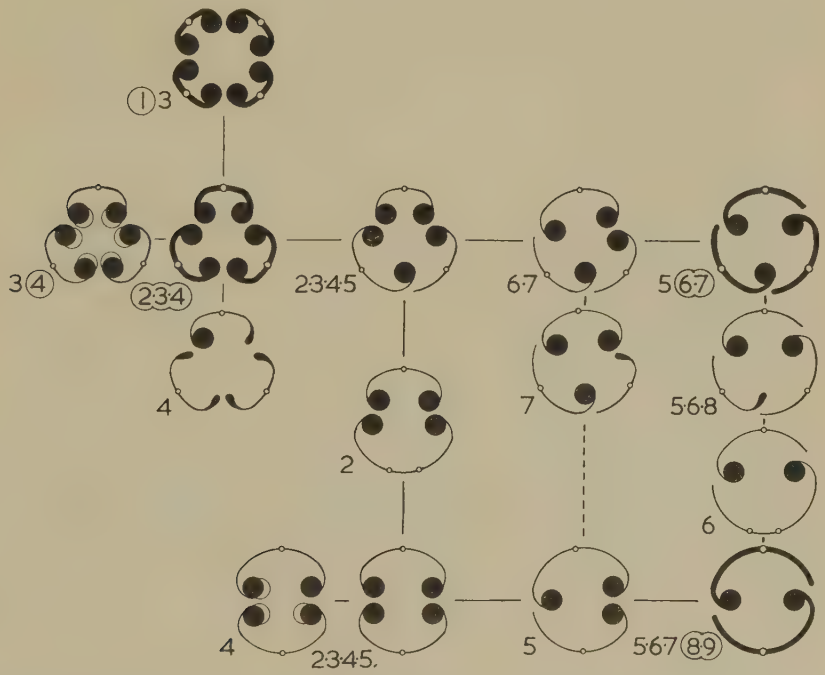

FIG. 19—Diagrams of the ovaries in *Melicytus* and *Hymenanthera*. Encircled figures indicate basic types.

1. *M. ramiflorus*
2. *M. macrophyllus*
3. *M. macrophyllus* × *M. lanceolatus*
4. *M. lanceolatus*
5. *M. lanceolatus* × *H. chathamica*
6. *H. chathamica*
7. *M. micranthus* and vars.
8. *H. novae-zelandiae*
9. Other *Hymenanthera* spp.

TABLE 1

	2n	Carpels (Modal Figures)	Ovules Per Carpel (Modal Figures)	Time of Male Degeneration
M. ramiflorus Forst.	32	4	2	prophase
M. macrophyllus A. Cunn.	32	3	2	meiosis
M. macrophyllus × *M. lanceolatus*	32	3	2	early prophase
M. lanceolatus Hook. f.	32	3	2, 4	tetrads
M. lanceolatus × *H. chathamica*	32	3	1, 2	early prophase
H. chathamica (F. Muell.) Kirk	32	3	1	meiosis
M. micranthus Hook. f.	64, 96	3	1	prophase
H. novae-zelandiae (A. Cunn.) Hemsl.	32	2	1	unknown
H. obovata Kirk	32	2	1	(hermaphrodite)
H. angustifolia R. Br. ex D.C.	32	2	1	prophase
H. angustifolia R. Br. ex D.C.	64	2	1	(hermaphrodite)
H. alpina (Kirk) W. R. B. Oliver	64	2	1	(hermaphrodite)
H. crassifolia Hook. f.	64	2	1	(hermaphrodite)

Cytology

SPECIES AND VARIETIES

The somatic chromosomes have mainly submedian to subterminal centromeres but are too small for detailed study.

Meiosis in pollen mother-cells is normal, all species and varieties studied being functionally diploid, irrespective of the degree of polyploidy.

In the tetraploid species of *Hymenanthera* (n = 32) there is pronounced secondary association of bivalents (see Beuzenberg and Hair, 1959, figs 21 and 26).

Two complexes have more than one chromosome number. *Hymenanthera angustifolia* has a diploid, dioecious race with few, small, narrow leaves on flexuous branches, and a tetraploid, hermaphrodite race with more and larger leaves on more rigid branches. The geographical distribution of these races is not known. *Melicytus micranthus* is a complex containing the tetraploid, larger leaved variety, *longiusculus* and the hexaploid, smaller leaved varieties *micranthus* and *microphyllus*.

HYBRIDS

a. *Melicytus micranthus* var. *longiusculus* (2n = 64) × *M. micranthus* var. *micranthus* (2n = 96).

Field observations at Prices Valley (Banks Peninsula) disclosed a very mixed population of *M. micranthus*, containing, in addition to the typical form, larger leaved plants identified as var. *longiusculus* and a whole range of plants connecting these extremes. The supposition that free hybridisation

occurs in this locality was confirmed by a cytological analysis of the large- and small-leaved forms and of the ten seedlings raised from one plant of var. *longiusculus*. Eight of the seedlings were pentaploid ($2n = 80$) (Fig. 22), and two tetraploid. So far, no meiotic material of the hybrids has been available.

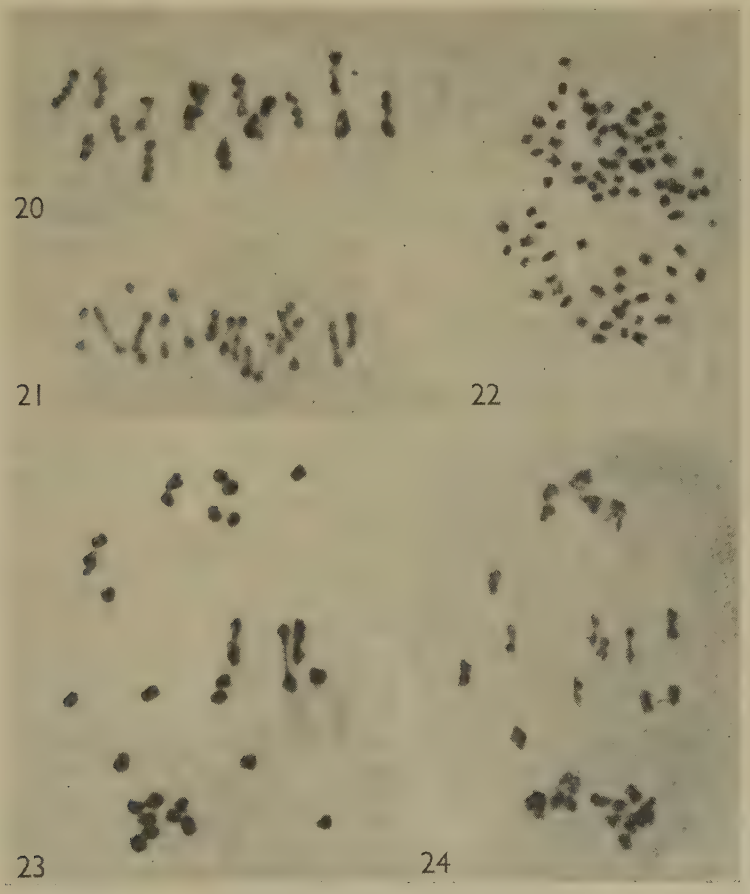

FIG. 20—*Melicytus macrophyllus:* degenerating bivalents. × 1,500.

FIG. 21—*Melicytus lanceolatus* × *Hymenanthera chathamica:* first meiotic metaphase; 16^{II}. × 1,500.

FIG. 22—*Melicytus micranthus* var. *longiusculus* × *M. m.* var. *micranthus:* mitotic metaphase; $2n = 80$. × 1,500.

FIG. 23—*Melicytus macrophyllus* × *M. lanceolatus:* first meiotic metaphase; $3^{II} + 26^{I}$. × 1,500.

FIG. 24—Ditto: late first meiotic anaphase; 7–11–14 distribution of half-bivalents and undivided univalents. × 1,500.

b. *Melicytus macrophyllus* (2n = 32) × *M. lanceolatus* (2n = 32)

Seedlings from a cultivated female plant of *M. macrophyllus,* isolated from males of that species but growing close to a male plant of *M. lanceolatus,* proved to be morphologically intermediate between these species, and were diploid.

Chromosome behaviour at meiosis was exceedingly irregular. Only 3 or 4, sometimes 5, bivalents were formed (Fig. 23) and the behaviour of the numerous univalents was variable: they were in part distributed, undivided, to the poles at first anaphase when they divided at the second division; or they could lag at the equator (Fig. 24) and divide either at first anaphase, or at the second division following partial restitution. Diverse behaviour of the unpaired chromosomes was reflected at the end of the second division, where uneven tetrads (50%), triads (25%), and dyads (25%), with or without micronuclei, were characteristic. The estimate of pollen fertility (by courtesy of Mr J. E. Herkert) was only 10%–15%.

c. *Melicytus lanceolatus* (2n = 32) × *Hymenanthera chathamica* (2n = 32)

Seedlings raised from a cultivated female plant of *Melicytus lanceolatus* proved to be diploid and probable intergeneric hybrids, the putative male parent, *Hymenanthera chathamica,* being the only possible source of pollen in the near vicinity. The presumed hybrids were indeed intermediate, both in leaf and in floral characters.

Meiosis in the male was quite regular (Fig. 21). According to Mr N. T. Moar (pers. comm.) the pollen is perfect.

DISCUSSION

Sex Differentiation

According to some recent interpretations, sex expression is controlled by a number of external and internal factors, which operate through changes in the local concentration of auxin. If the auxin level exceeds a certain threshold value, an initially male phase is followed by a female phase. (Heslop-Harrison, 1957a, 1957b). This gradient of sex determination is reflected in the developmental pattern (spatial and temporal) within a hermaphrodite flower, and, similarly, in the sequence of sex types along a monoecious flowering shoot. This view would explain the following observations in the Hymenantherinae:

a. The anthers are well developed with the sporogenous cells sharply defined, before ovular development is even apparent.

b. Late and almost mature flowers in some male plants show much more extensive female development. The bisexual potentiality in a genotypically male plant can be realised, during the growth, through a gradual increase in available auxin, especially if the sex balance is near equilibrium. This modification has a parallel in and may be of the same kind as such phenomena in other plants as: the seasonal modifications in female fertility, the temporal variations in sex ratios, the time of the female phase in a

monoecious flowering shoot, etc. In the present case it was not possible to evaluate the factors, other than the time component, initially responsible for the upward shift in auxin supply.

c. As the flowering season progresses, male degeneration is found to occur at an earlier stage. Collapse of the stamens appears to coincide with the differentiation of the megaspore mother-cell (Figs 2 to 13, 14; cf. Whyte, 1929). It could then be inferred that, relative to the male phase, the female phase is progressively advanced in time, due again to a gradual upward shift in auxin availability.

d. A reduction in the number of stamens and associated floral parts in a male plant of var. *microphyllus* of *Melicytus micranthus* was associated with greater female development. A similar inverse correlation between the number of stamens and their developmental state, and gynoecial development, has often been reported in literature, more recently, for example, by Schlenker (1953) in *Populus,* and by the Heslop-Harrisons (1958) in *Silene.*

Male degeneration follows a sequence comparable with that described in cytoplasmic male-sterility. Collapse of the pollen mother-cells has been attributed to nutritional disturbances which in turn are conditioned by an acceleration, retardation, or cessation of tapetal activity (Harte and Bissinger, 1952; Welzel, 1954; Kobabe, 1958; and others). It is suggested in the present study however, that abnormal tapetum activity is only one of the events associated with male degeneration and not its primary cause. It has been shown that the anthers in the two sexes differ in the middle layers long before the first signs of disorganisation become apparent. It was shown also that dissolution of the tapetum may precede collapse of the pollen mother-cells in some species, or may be greatly delayed in others. Whatever the basic cause of degeneration, its many manifestations, embracing almost every part of the abortive anther, show no consistent relationship in time or in space. On the present evidence, it is therefore unwise to attempt the construction of a unified sequence of cause and effect.

Cytotaxonomy

A detailed re-examination of the diagnostic characters currently used to separate *Melicytus* and *Hymenanthera* casts some doubt on the validity of such a distinction. The characters concerned are very variable, both within and between species, and the pattern of variability is an overlapping one which links the genera as well as their constituent species by a progressive series of fusions and reductions in the floral organs (Table 1; Figs 18–19; Table 2).

Pollen characters are similar throughout the Hymenantherinae (Mr N. T. Moar, pers. comm.), and cannot be used to define generic limits, if such indeed exist.

Further light on this question is shed by the cytological data. The two genera cannot be separated on the grounds of basic chromosome number, size of chromosomes, or other detectable features of chromosome mor-

phology. Further, they are closely linked by hybridisation between the borderline species, *Melicytus lanceolatus* (which has the staminal characters of a *Hymenanthera*), and *Hymenanthera chathamica*. The strength of this link is reflected in perfect meiotic pairing and perfect pollen in the hybrid. Whilst it is true that pairing relationships do not necessarily provide the last word on genetic homologies, and should be supplemented by F2 data, it is clear in the present instance that the parental species are by no means distantly related.

TABLE 2

Melicytus According to Melchior (1925)	*Hymenanthera* and Cheeseman (1925)	*Exceptions*
Anthers free	Anthers coherent	*M. lanceolatus* (*H. chathamica* intermediate)
Ovary with 3 to 5 placentae*	Ovary with 2, rarely 3 or 4 placentae**	*H. chathamica*
More than one ovule per carpel	One ovule per carpel	*M. micranthus*

*Actual numbers found: 2, 3, 4.

**Actual numbers found: 2, 3.

As might be anticipated, the species show a general trend from a tall habit at the diploid level, to a smaller, more rigid, divaricating habit with reduced leaves, fewer carpels and connate stamens, at diploid, tetraploid, and hexaploid levels. The small-leaved race of *Hymenanthera angustifolia* is an extreme at the diploid level, and may well have been an immediate ancestor of the tetraploid species of *Hymenanthera*. These three tetraploid species have in common a greater or lesser degree of secondary association of bivalents at meiosis. The significance of this is not clearly understood, but it tends to suggest that the tetraploids arose recently through amphidiploidy at a sub-specific level.

A change in ploidy in the Hymenantherinae is not necessarily associated with a change in breeding systems; the change from bisexuality to unisexuality has taken place mainly in the morphologically more primitive species.

It is of interest to note that the suggestion by St. John (1952) of closer affinity with the Hymenantherinae for *Isodendrion*, which had previously been placed with different subtribes by Melchior (1925), is further strengthened by the present study. With the exception of deciduous stipules and perhaps sessile stamens in *Melicytus*, all of the remaining differences listed by St. John have been found here to vary widely within the Hymenantherinae and thus cannot be used as consistent criteria for separating *Isodendrion* from *Melicytus* and its relatives.

ACKNOWLEDGMENTS

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CONTRIBUTIONS TO THE QUATERNARY HISTORY OF THE NEW ZEALAND FLORA

4. POLLEN DIAGRAMS FROM THE WESTERN RUAHINE RANGES

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(Received for publication, 24 February 1961)

Summary

Pollen diagrams from the Mokai Patea and Whanahuia ranges in the Ruahine mountain system are discussed, and it is thought that the deeper peats were formed early in the second post-glacial period and that the shallower peats began growth near the close of this period. Correlation of the pollen diagrams, especially in the shallower peats, is made easier by the presence of recognisable layers of Taupo and Waimihia pumice. A marked increase of *Dacrydium bidwillii-biforme* pollen between the pumice layers is correlated with the presence of *Dacrydium biforme* wood in peats and soils above the present timber line, but it is difficult to decide what factor was responsible for the extension up slope of this species. *Nothofagus menziesii* and *Ascarina* sp. pollen occur intermittently through most profiles, and it is suggested that these species may have a long history in the area.

INTRODUCTION

Bogs on the Mokai Patea Range were examined in February 1951, and an account of their vegetation and peat types has been published by the author (1956). The results of pollen analyses were not reported as it was hoped to return for more detailed work, a hope not realised until March 1959, when the Mokai Patea Range was revisited with Messrs A. P. Druce and I. A. E. Atkinson, Botany Division, Department of Scientific and Industrial Research. In the same month bogs on a western spur of the Whanahuia Range were examined by Mr Druce and the author.

The Mokai Patea Range is the most northerly and the Whanahuia Range is the most southerly of three ranges lying between 39° 40′ S and 39° 80′ S, three to five miles west of the main divide of the main Ruahine system. These two ranges are about fourteen miles apart and are separated by the Hikurangi Range (Fig. 1). Rongotea, the highest peak in the Mokai Patea Range rises to 5,144 ft, and two lesser peaks, Mokai Patea and Colenso, rise to 3,969 ft and 4,613 ft respectively. The peats examined lie on the main ridge, which has a broad rolling surface rising gradually from the saddle east of Colenso, to Rongotea. The Whanahuia Range is more dissected and the highest point rises to 5,562 ft. Peat samples were collected from small bogs on a spur which was formerly a ski-ing ground, at altitudes between 4,400 ft and 4,600 ft.

FIG. 1—Location of the Mokai Patea and Whanahuia Ranges in the western Ruahine Range system. The locality in which the peats were samples are indicated thus: A. Mokai Patea Bore No. 1, 1959. B. Mokai Patea Erosion Hole, 1959. C. Mokai Patea Bores No. 1, No. 5, 1951. D. Whanahuia Bores No. 1, No. 2.

PRESENT VEGETATION

The peats on both ranges lie above the present timber line which on the Whanahuia Range is at about 4,200 ft; on the Mokai Patea Range the timber line varies in altitude considerably, but it is generally below 4,300 ft. Between 4,400 ft and 4,600 ft, on the Whanahuia Range, wherever the soil surface has been disturbed and eroded, and in the peats, numerous remains of trunks and roots of *Dacrydium biforme* testify to the presence of former forest in an area now characterised by tussock-grassland. Similar remains occur on the Mokai Patea Range, Mr N. L. Elder (pers. comm.) having found logs as high as 4,700 ft, but their presence was not demonstrated in the peat which first occurs at about 4,500 ft.

The vegetation of the Ruahine Ranges has not yet been fully described, but a list of species from the area (Aston, 1914) and comments by Cockayne (1928) provide a useful background to the primitive vegetation of the region. Recent detailed work by Messrs Elder, Druce, and others (unpublished) has shown that the vegetation of the Ruahine Range is very varied.

The lowlands generally were clothed with podocarp-dicotyledonous forest, as were the lower slopes of the ranges. On the Whanahuia Range *Nothofagus fusca* forest was predominant, with *Libocedrus bidwillii* forest above it. A general description of the subalpine forest (Cockayne, 1928) approximates that of the Whanahuia Range and is here quoted: "Close to the timber-line the forest becomes very low (scrub-forest), and it is closely related to bog forest and subalpine scrub. Its small trees are *Libocedrus bidwillii, Dacrydium intermedium, D. biforme, Phyllocladus alpinus, Griselinia littoralis* and *Dracophyllum longifolium*". This statement should be modified since no *Dacrydium intermedium* was found on the Whanahuia Range, and according to Mr Druce (pers. comm.) none occurs in the Ruahine Ranges. Further, Mr Druce has also informed the author that *Dracophyllum longifolium* var. *septentrionale* is found only in the southern Ruahines. *Nothofagus solandri* var. *cliffortioides* occurs in the subalpine forest and extends to the timber line. The vegetation of the upper forested slopes of the Mokai Patea Range differs in that *N. solandri* var. *cliffortioides* is the characteristic species.

Although fires on both ranges have modified the timber line vegetation, and on the Mokai Patea sheep have been grazed on the tussock grassland, there are differences between the two ranges which cannot be explained in terms of fire, or grazing. *Libocedrus bidwillii* occurs in quantity on the Mokai Patea Range but it is not so widely, or as continuously, distributed as it is on the Whanahuia Range. Logs of *L. bidwillii* lying under beech forest indicate that it has been more abundant in the past. *Nothofagus menziesii* is recorded from the Mokai Patea Range, but it is absent from the Whanahuia Range. On both ranges *Olearia colensoi* extends as widely scattered shrubs well above the timber line, but only on the Whanahuia Range does it form a continuous timber line scrub.

A general account of bog vegetation on the Mokai Patea has been published (Moar, 1956), and this can apply also to the Whanahuia Range, except that peat development on the latter range is not so widespread and the bog vegetation not as varied. On both ranges some peats have ceased to accumulate and are now hidden by a dense growth of *Danthonia* sp.

PEAT PROFILES

Three distinct layers of pumice occur in the Ruahine peats, but not all of them were recorded in each profile. The youngest, a part of the Taupo lapilli, was found in each profile examined, the second youngest, a part of the Waimihia lapilli, was recorded in four profiles, and the oldest, an unidentified banded layer, occurred in the deep Mokai Patea bore No. 1, 1959 (Figs. 1, 2). The Taupo pumice (Baumgart, 1954) has an age, calculated by the radio carbon technique, of 1,820 ± 150 years old (Fergusson and Rafter, 1953, 1957). Baumgart (1954), considered that the Waimihia pumice was considerably older than 3,000 years, but recent work indicates that it may be no more than about 3,500 years old (Fergusson and Rafter, 1959; pers. comm. J. Healy, C. Vucetich). In addition, fine black volcanic ash of Ngauruhoe origin was found near the surface of peat in an erosion hole (Fig. 2).

Layers of volcanic ash or pumice found in peats provide fixed points for correlation when they can be recognised over a wide area, and in Fuego-Patagonia, Auer (1948, 1958) was able to divide the post-glacial into four chronological sequences based on the occurrence of three recognisable layers of volcanic ash in many bogs. Hori (1957) has used a succession of ash layers of known age and origin as one means of calculating the rate of peat accumulation in some Japanese bogs. Unfortunately this method does not help to calculate accurately the ages of the Ruahine peats since rates of peat accumulation, especially between the two identified pumice layers, vary so much. However the shallower peats are unlikely to be more than 4,000–5,000 years old, but ages ranging from 8,000–12,000 years can be calculated for the two deep Mokai Patea peats, depending on which of the pumice layers the calculations are based.

The pollen diagrams (Figs 1, 2) show no rapid changes, but there is, from the base, an overall decrease in *Podocarpus** pollen with an accompanying increase in *Nothofagus* pollen.

Podocarpus pollen never falls to an insignificant level and in several profiles there are marked fluctuations between this genus and *Nothofagus* extending through considerable depths of peat before *Nothofagus* pollen becomes dominant in the upper part of the profile. Each profile, with the exception of the Mokai Patea erosion hole, thus illustrates a general succession, *Podocarpus* → *Podocarpus* – *Nothofagus* → *Nothofagus*.

This trend suggests that peat formation is contemporaneous in all profiles, but it is obvious that the two deep Mokai Patea profiles are the oldest and their calculated ages imply that they could have been formed at some time near the close of the late glacial and presumably in the first post glacial period of Cranwell and von Post (1936).

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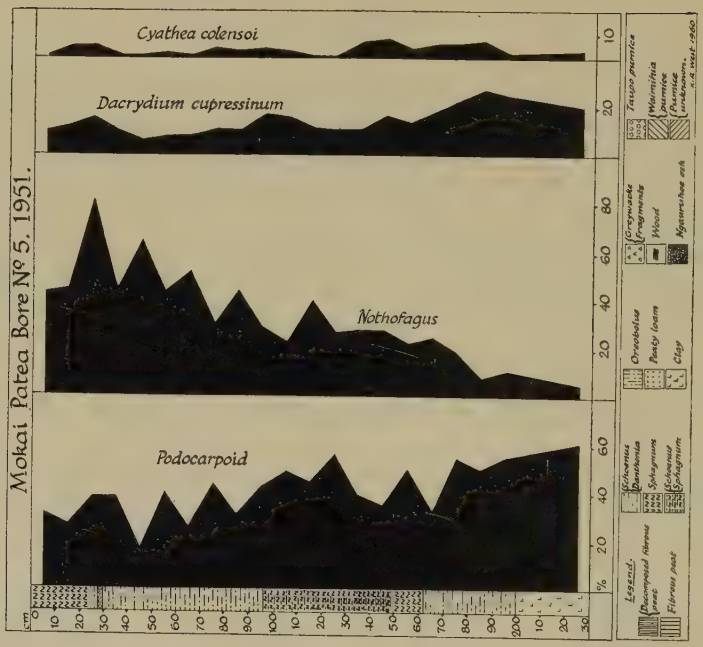
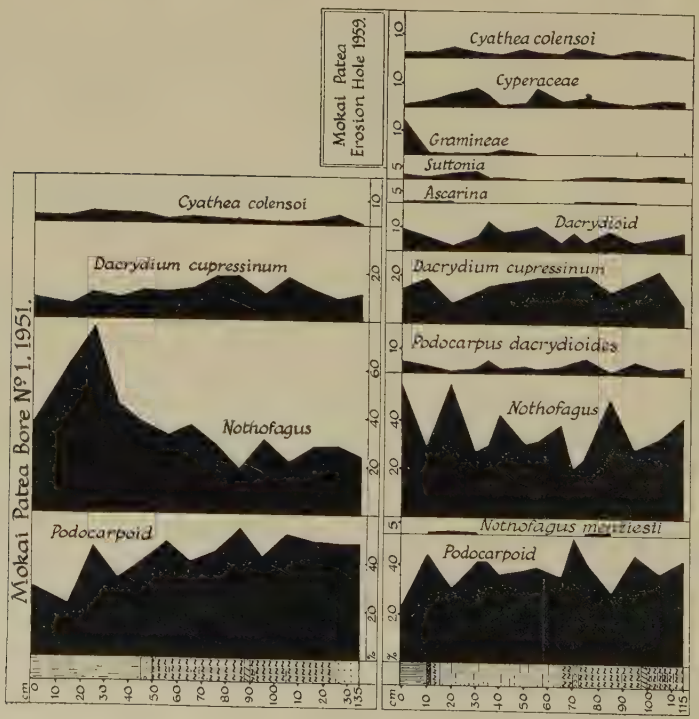
*Because of difficulties in identification associated with the process of fossilisation, the pollen of *Podocarpus* species have been presented as "*Podocarpoid*" in the pollen diagrams.


Mokai Patea Bore No 5, 1951.
Cyathea colensoi
Dacrydium cupressinum
Nothofagus
Podocarpoid
Legend:
Decomposed fibrous peat
Fibrous peat
Sphagnum
Sphagnum fibrous peat
Ornthoptera
Peaty loam
Clay
Greywacke fragments
Wood
Ngauruhoe ash
Taupo pumice
Warmiha Hamilton Pumice (unknown, c. 14,000-16,000)
cm
%


Mokai Patea Bore No 1, 1951.
Cyathea colensoi
Dacrydium cupressinum
Nothofagus
Podocarpoid
Mokai Patea Erosion Hole 1959.
Cyathea colensoi
Cyperaceae
Gramineae
Suttonia
Ascarina
Dacrydioid
Dacrydium cupressinum
Podocarpus dacrydioides
Nothofagus
Nothofagus menziesii
Podocarpoid
cm

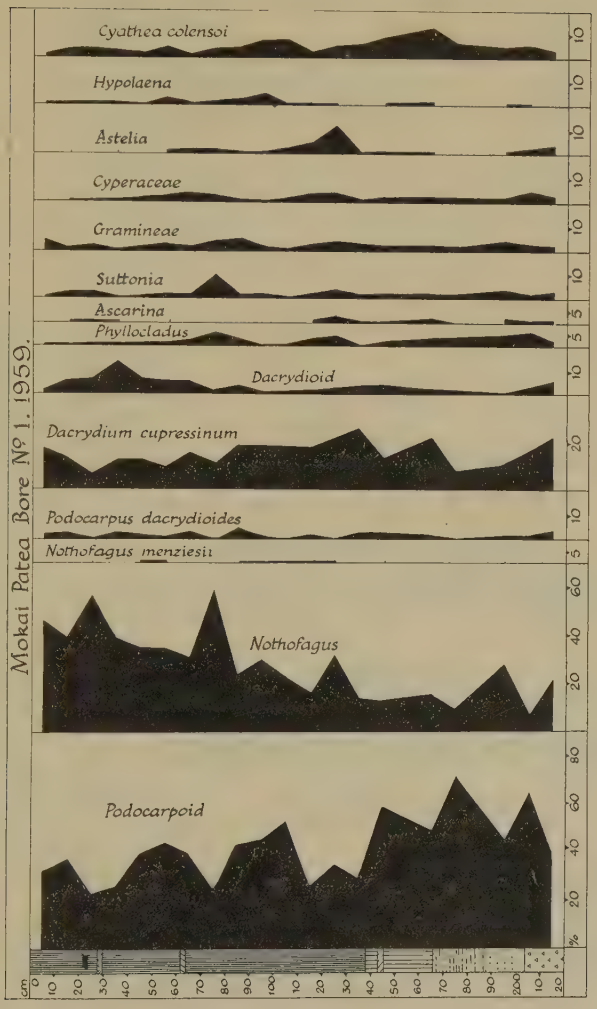
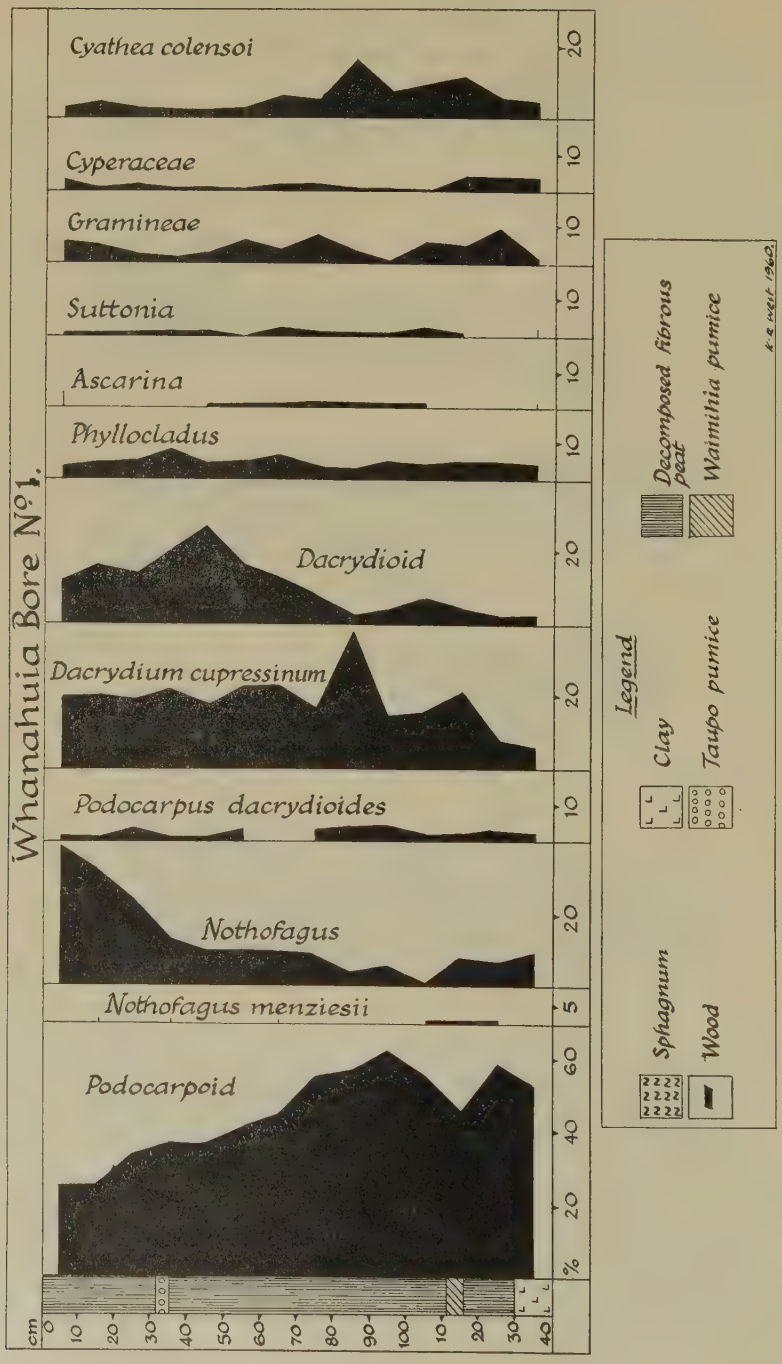


FIG. 2—Pollen diagrams of the four profiles from the Mokai Patea Range.

DISCUSSION

Willett (1950) states that periglacial conditions extended over the Ruahine Ranges in the late Pleistocene, and this statement appears to be confirmed by Brodie (1957) who shows that subalpine conditions existed near sea level at Wellington at that time. According to Willett (1950) subalpine tussock would have replaced forests in the mountain region of the central North Island. Although such severe climatic conditions would not have existed at or near the close of the late glacial, it is unlikely that forest recovery would be so rapid that the pollen spectrum was dominated by *Podocarpus*


Whanahuia Bore No 1.
Cyathea colensoi
Cyperaceae
Gramineae
Suttonia
Ascarina
Phyllocladus
Dacrydioid
Dacrydium cupressinum
Podocarpus dacrydioides
Nothofagus
Nothofagus menziesii
Podocarpoid
cm
%
Legend
Clay
Taupo pumice
Decomposed fibrous peat
Waimihia pumice
Sphagnum
Wood

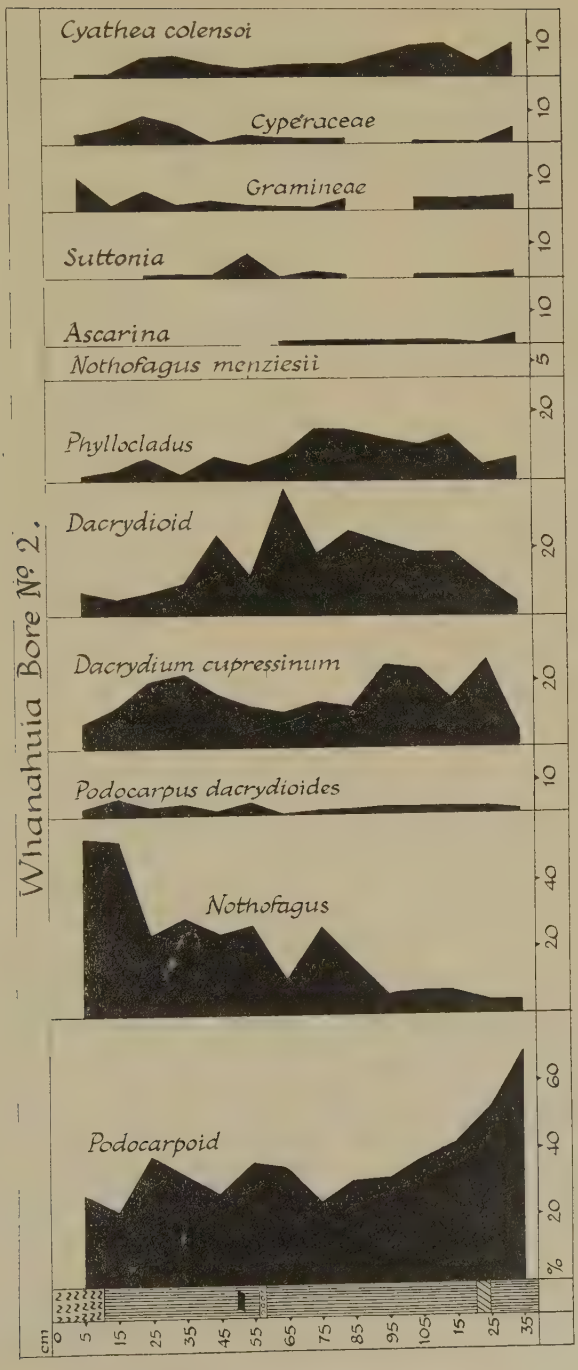


FIG. 3—Pollen diagrams of two profiles from the Whanahuia Range.

species. The high frequencies of *Podocarpus* pollen in the lower parts of the profiles does not support the implication that the peats are late glacial, but rather, indicates that the peats date from the second post-glacial period, the period of *Podocarpus* maximum (Cranwell and von Post, 1936), and comparison with the similar diagrams for Wallaceville (Harris, 1951) supports this view. The present impression then is that these two deep peats began formation in the earliest stages of the second post-glacial period.

The pollen diagrams for the shallower peats show that these also originated during the second post-glacial period. The position of the Waimihia pumice layer, and the ages calculated from this layer indicates that these peats cannot be any more than 5,000 years old. Peat accumulation therefore began in the later stages of the second post-glacial period.

In the more detailed Mokai Patea and Whanahuia profiles "Dacrydioid"* pollen increases in frequency and reaches a maximum between the Taupo and Waimihia pumice layers. The ages of both pumice layers indicate that they were deposited during the third post-glacial period so that the trend from both areas may be contemporaneous. The interest in this lies in the fact that the timber line is apparently not a stable one and the field evidence of *Dacrydium biforme* wood in the peats and shallow soils shows that this species was once common at altitudes up to 500 ft above the present timber line. The pollen record indicates that this upward extension, and subsequent retreat, occurred between 2,000 and 3,000 years ago as dated by the pumice layers.

Elder (1959) considers that the discontinuous forest pattern in the Ruahine Ranges "can fairly be attributed to the drowning out of forest by the formation of peat, presumably marking a recent climatic change to cooler, wetter, and/or cloudier conditions. . . . ". It is generally held that the third post-glacial period was marked by a cooler, drier climate which does not agree with an upward movement of a sub-alpine species such as *Dacrydium biforme*. The deeper peats contain no recognisable remains of forest species, and in the shallower peats wood remains do not extend to the bottom. Further, since peat formation is now less active than formerly (Moar, 1956), it is difficult to agree, on present evidence, that climatic conditions altered so much that peat formation drowned out the forest. So far as the present results permit speculation it is better to regard the change as a result of a slight temperature variation, and not to invoke increases in moisture. Whatever the cause, the increase in *Dacrydium* above the present timber line cannot possibly be contemporaneous with the recent changes postulated for the South Island by Holloway (1954).

It is interesting to note that *Ascarina* pollen occurs intermittently through most of the profiles, especially since the recent discovery of *Ascarina lucida* in the Hutt River catchment (pers. comm. A. P. Druce and I. A. E. Atkinson) indicates that the distribution of this species is not thoroughly known. It is not recorded from the Ruahine Ranges. The record of *Nothofagus menziesii* in the peats indicates that this species has been in the area for a long time.

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*Included under "Dacrydioid", are the pollen grains of *Dacrydium biforme* and *D. bidwillii* which are not easily separated.

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BORON IN NEW ZEALAND COAL ASHES

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(Received for publication, 17 February 1961)

Summary

A new method of boron analysis of coal ash is described, similar to that used in the determination of boron in glass. The boron contents of some New Zealand coals, and their ashes, are presented, showing them to be among the richest in the world. Boron content is shown to be related to, or affected by: ash content of coal, calcium content of coal ash, rank of coal above sub-bituminous, the major structural trends of the Waikato region, and (in the case of peat) proximity to active hot springs. No relation is obvious with: items of the proximate and ultimate analyses (excepting ash content), coal type, location within the broad area of a single mine, stratigraphic differences of up to 100 ft, or major differences of depositional environment as between Eocene-Oligocene and Miocene coals of the North Island.

It is concluded that hot-spring waters can enrich nearby peat in boron. A similar mechanism for enriching coals, subsequent to their deposition, appears the most likely of several hypothetical sources, but the evidence is insufficient for a definite conclusion, especially in view of the possibilities of derivation of boron from percolating sea water.

INTRODUCTION

Some 18 years ago, several Waikato coal ashes were analysed at Dominion Laboratory by Mr F. T. Seelye, and were found to contain boron, in some cases as much as 4½% boron trioxide. Further investigation of many New Zealand coalfields showed that South Island ashes contained less than 1% B_2O_3, with the exception of Burnwell (Reefton, 2·73%), Kaitangata (1·40%), Wangaloa (1·08%), and Blackball (1·07%); but those from the North Island were generally richer, being between 2% and 4·8% (maximum at MacDonald Mine) in the central Waikato coalfields, between 1% and 2½% in the south (Mangapehi, Mokau, and Tatu), and 0·7% B_2O_3 in Northland (Kamo Mine). Rafter (1945) briefly mentioned these high values, and suggested a connection with the boron content of hot spring waters of the central North Island thermal area.

Goldschmidt (1935) had previously recorded that, for coal ashes rich in boron, the average amount present was 0·06% and the maximum 0·3% (i.e., 0·2% to 1·0% B_2O_3). These figures were said to indicate a concentration 200 to 1,000 times greater than the average for the earth's crust. Headlee (1953) considered that the concentration was 10 to 185 times. Coal ashes rich in boron have been recorded by Gibson and Selvig (1944) from North Dakota (0·67% B_2O_3), Germany (0·30%), Russia (up to 1%), and Newcastle (England, 1%). Twelve South African coals, listed by Kunstmann and Harris (1954), have boron trioxide contents ranging from 35 p.p.m. to 193 p.p.m. The comparable average figure for Pukemiro Mine

(Waikato) is 1,390 p.p.m., and one sample contained 1,500 p.p.m. The ash contents of the coals from North Dakota, etc., were not stated by Gibson and Selvig, and the boron content cannot therefore be assessed in p.p.m.; but it may reasonably be inferred that the coal ashes of New Zealand in general, and of the Waikato coalfields in particular, are some of the richest in boron in the world.

A recent project was undertaken to investigate further the geographic and stratigraphic distribution of the boron, in an attempt to learn more of its origin. The fullest use was made of the earlier work, and new samples, which seemed most likely to be significant, from the Waikato area alone, were chosen. Each sample, in itself, was truly representative of the mine or seam from which it was obtained, and it is considered that the total samples available are sufficient to show, at least, the major differences in concentration.

METHOD OF BORON ANALYSIS

The method of analysis for the determination of boron used 16 years ago was to distill the coal ash with methyl alcohol, in the presence of hydrochloric acid and calcium chloride. The resulting methyl borate ($B(OCH_3)_3$) was treated chemically and finally titrated with standard caustic soda solution after the addition of mannitol.

It was thought that alternative methods would be worth investigating. Those of Kunstmann and Harris (1954), which gave a greater accuracy than the $\pm$ 0·02% B_2O_3 required here, and of Norwitz and Codell (1954), which used a cation exchange column to determine boron in titanium alloys, were considered before it was decided to try out a pH method similar to that used in the determination of boron in glass (Hollander and Rieman, 1946). The method finally adopted is given below.

The coal samples were ashed at 800°C in platinum dishes without the addition of alkaline material, such as calcium oxide, as it was considered that the basicity of the ashes would be sufficient to prevent loss of boron on ignition. Half a gramme of ash, ground to pass a 200 B.S. sieve, was fused with sodium carbonate, the melt dissolved in 6N HCl, and iron, aluminium and silica precipitated by the addition of sodium hydroxide solution. After the removal of carbon dioxide, the solutions were filtered and washed, giving a filtrate of about 190 ml.

When they had attained room temperature, the filtrates were brought to a pH of 6·8–7·0 with a Cambridge pH meter. Mannitol was added and the solutions titrated with standard sodium hydroxide solution until the pH was again 6·8–7·0. The amount of sodium hydroxide required is a measure of the amount of boron present in the filtrate. If more than 1% of B_2O_3 were present, a second precipitation was carried out, the two filtrates always being titrated separately. A "blank", obtained by running a boron-free coal through the entire procedure, was of the order of 0·2 ml sodium hydroxide solution (0·03–0·04% B_2O_3).

The sodium hydroxide solution used (approximately N/40) was standardised by adding aliquots of a standard boron solution to samples of the boron

free coal ash, and carrying the samples through the entire procedure. Duplicate determinations agreed to within 0·10–0·15 ml sodium hydroxide solution, i.e., to within 0·02% B_2O_3.

The removal of iron and aluminium by the use of a cation exchange column, Zeo Karb 225, was tried. However, it required so much washing that a large volume of boron-containing solution resulted which had to be reduced by evaporation. There was no gain in time and there was the possibility of loss of boron through volatility in the steam. Hence its use was discontinued.

Although Norwitz and Codell (1954) stated that the stability of the boric acid-complex falls off rapidly with rising temperatures and recommended that the temperature of the solution of the titration stage be maintained between 10° and 15°C, these conditions were not purposely adhered to with this series of coal ashes. During the summer months when the method was being tried, an attempt was made to keep the temperature of some of the solutions down by standing the beakers in iced water; no differences were apparent, within the accuracies sought, between the cooled solutions and those at room temperatures. The room temperatures, when the final determinations were carried out, were usually about 16°C.

A very useful "spot" test was used which proved invaluable when working out the procedure of the analysis, e.g., to know when beakers had been washed out sufficiently or if a precipitate had been completely washed. The mannitol was purified for this test by being recrystallised from a solution neutral to bromo-thymol-blue. A drop of the solution under test was put in a depression of a spot plate followed by a drop of this indicator and sufficient dilute sodium hydroxide to render it green in colour. On adding a small lump of the purified mannitol, a yellow ring appeared if boron were present. The speed of formation and intensity of coloration gave a very good indication of the relative amounts of boron present in the wash waters, etc. According to Vogel (1947) the concentration limit of this test is 1 in 30,000,000.

In the list of analyses, a trace signifies about 0·01% B_2O_3. To make certain boron was not lost in the ashing process, the analyses of samples 7972 and 7973 were repeated, the coals being ashed in the presence of calcium carbonate. Again, no boron was found in the resulting solutions. A recent Pukemiro sample (slack through $1\frac{1}{8}$ in. screen) was analysed to compare the result with that of 15 years earlier. The figure of 4·56% B_2O_3 in the ash is closely similar to 4·54% in the ash of a 1940 run-of-mine sample.

NATURE OF THE BORON COMPOUNDS IN NEW ZEALAND COALS

The exact form of boron in coal, or in a coal ash, is not known. Of the possible boron-containing minerals, two, borax and kernite (both sodium borates) dissolve slowly in cold water and much more readily in hot water. Others, such as colemanite (a calcium borate) and ulexite (a mixed calcium and sodium borate) are soluble in dilute acids. Mr T. A. Rafter found

small amounts of boron in mine waters from the Renown, Pukemiro, and Glen Afton Collieries. Also, on heating a Pukemiro R.O.M. sample, with water, he found over 50% of the total boron was extracted; and, on heating a laboratory-prepared ash from the same sample, about 90% of the boron was water soluble. However, on repeating the experiment with a sample from the Pukemiro ash dump (C.S. X19), the boron was found to be much more difficult to get into solution.

From this, it may be inferred that some of the boron in a coal could be present as a sodium borate, a soluble form, but on combustion the nature of the minerals change. Mild heating (to 800°C) can increase the proportion which is water-soluble, but further heating, as in a commercial boiler, can produce an ash that requires acid to remove an appreciable amount of the boron. In any proposal to extract boron from the ash of a commercial plant, consideration would have to be given to the use of acid; this would be costly as a large proportion of the acid would be used in neutralising the high lime content of Waikato coal ashes.

ANALYSIS OF RESULTS

Tables 1 and 2 present all known boron contents of coal ashes from the North Island and South Island respectively. The geographic distribution of mine samples is illustrated broadly in Fig. 1. The following sections deal primarily with coal and peat from the North Island where the higher boron contents were recorded, but South Island samples are also discussed.

Ultimate and Proximate Analyses

The proximate and ultimate analyses have been determined for all North Island coals listed in Table 1, and the seven examples from Rotowaro Mine (Table 3) are sufficient to show that, of all the items in these analyses, only the ash content of a coal appears to be related in any way to the boron content of its ash. This relationship is shown to be inverse by plotting values for those mines from which more than one analysis is available (Fig. 2), and is best explained by assuming that the boron content of coal is very broadly constant within the area of a single mine. Table 4 implies the probable validity of this assumption by showing that far greater differences of boron content can exist between coal from different mines than do exist between coals from a single mine. As it is therefore likely that a coal's boron content remains broadly constant regardless of its ash content, boron contents are best expressed in this discussion as parts per million (p.p.m.) of coal rather than as a percentage of coal ash.

Ash Fusion Temperature and Lime Content

Officers in the Dominion Laboratory have studied the physical and chemical properties of New Zealand coal ashes in some detail, and a number of results were recorded in cyclostyled form in Coal Report 249, of Dominion Laboratory, D.S.I.R. This report shows that the boron content bears little relation to ash fusion temperatures (Fig. 3), which is surprising in view of the well known fluxing effect of borax.

TABLE 1—Localities, Boron and Ash Contents of North Island Coal Samples, Grouped According to Age.

Age of Sample	Details of Locality	Grid Reference	Field No.	Analysis C.S. No.	Ash %	Determined B_2O_3 in Ash (%)	Calculated B_2O_3 in Coal (p.p.m.)
Holocene (Recent peats)	Whangamarino Swamp, top 3 ft peat	N52/606024	236A	7975	14·4	? trace	10
	As above, compressed by filling	,,	236B	7976	10·2	? trace	10
	Ohinewai, Mawston's property, in hot spring area	N52/668877	245	9089	53·1	0·13	690
	As above, peat near hot spring	N52/669877	244	9090	65·1	0·07	460
Upper Pleistocene (Hawera)	Hamilton. Waikato River bank below Hospital Hill. 2 in. peat at base of Hinuera sands	N65/803450	205	7981	50·3	? trace	50
Pliocene (Lower Wanganui)	Whangamarino Station, 3 ft lignite in drillhole, 13 chains NW	N52/626005	234	7973	57·4	? trace	60
	Paddy Road, Whangamarino. Lignite in railway cutting	N52/643964	235	7974	47·3	Not found	..
Miocene (Southland Series) (Mokau Coal)	Mokau (Stockman) Mine, Mokau River	N91/330370	90	F4751	4·8	2·33	1120
	Tatu Mine, Ohura. R.O.M., 1941	N100	79	418	9·7	1·28	1240
? Oligocene (? Pareora Series)	Pokeno Railway Cutting, 1 mile north of Kellyville Crossing. Platy coal fragments in Otaian sandstone	N48/552116	201B	9215	7·5	0·33	250
Eocene (Upper Arnold)	Pokeno Railway Cutting, as above						
	Coal pebbles in Otaian sandstone	N48/552116	201A	9214	5·0	1·02	510
	Maramarua Coalfield Drillhole 1773 Seam 1,570 ft below sea level	N48/676127	231	7246	4·3	2·04	880
	Kopuku Opencast. R.O.M., 1950	N52/678096	212	5922	4·7	1·23	580
	As above. 1 ft of seam roof (carbonaceous mudstone).	N52/678096	238	7977	81·5	Not found	..
	As above. 1 ft coal, top of seam	,,	237A	7978	10·3	0·76	780
	As above. 1 ft coal, middle of seam	,,	237B	7979	2·9	1·45	420
	As above. 1 ft coal, bottom of seam	,,	237C	7980	3·2	1·65	530

	Kimihia Opencast. Slack –¾″	N56/693772	328	7573	4·1	1·48	610
	Rotowaro No. 1 Mine. Top 5′ 8″ of seam	N56/588694	12A	300	4·0	2·08	830
	As above. Middle 5′ 11″ of seam	,,	12B	301	1·9	2·53	480
	As above. Bottom 9′ 11″ of seam	,,	12C	302	2·6	3·42	890
	Pukemiro Mines. R.O.M., 1940	N56/569680	11	299	3·3	4·54	1500
	As above. Slack, 1940	,,	37	346	3·7	3·90	1440
	As above. Slack -1⅛″, 1954	,,	324	7569	2·7	4·56	1230
	Renown Mine, R.O.M., 1940	N56/560746	35A	339	3·4	4·38	1490
	As above. Slack, 1940	,,	35B	340	3·7	3·71	1370
	MacDonald Mine, R.O.M., 1940	N56/558720	1	286	2·8	4·80	1340
	Glen Afton and MacDonald slack	N55	6	345	3·6	3·92	1410
	Glen Afton Mine, R.O.M., 1940	N55/547685	5	285	4·3	3·02	1300
	Hetherington Road, Ruawaro. Coal outcrop on Smith's property	N55/502760	205	9091	10·8	0·84	910
	Wilton Mine, R.O.M., 1940	N56/574580	44A	359	4·8	2·83	1360
	As above. Slack, 1940	,,	44B	360	5·3	2·66	1410
	Whatawhata Mine, R.O.M., 1950	N65/607441	204	4401	4·9	2·41	1180
	Mangapehi Mine, R.O.M., 1940	N92/895585	18	380	6·4	1·91	1220
	As above, R.O.M., 1941	,,	23	414	6·3	1·72	1080
	As above, R.O.M., 1942	,,	24	464	7·6	1·60	1220
	Char. Rotowaro Carbonisation Works	N56/various	162	347	7·6	2·36	1790
Eocene (Arnold Series)	Rotowaro Mines, R.O.M., 1940	N56/various	19A	313	4·4	2·25	990
	As above. Slack, 1940	N56/various	19C	315	4·7	1·96	920
Eocene (Lower Arnold)	Kamo Mine, R.O.M., 1940	N20/820020	11	375	9·1	0·68	620
	Alison No. 1 Mine, R.O.M., 1940	N56/585709	22	320	2·4	2·48	600
	Rotowaro No. 3 Mine. Top 5′ 7″ of seam	N56/587693	18A	310	3·5	2·57	900
	As above. Middle 4′ 5″ of seam	,,	18B	311	2·6	3·36	870
	As above. Bottom 7′ 3″ of seam	,,	18C	312	2·7	3·11	840
Upper Jurassic to Lower Cretaceous ("Port Waikato plant beds")	Coast south of Port Waikato between Huruwai and Waikawau Stream 1 in. of coal	N51/242875	201	7972	18·5	Not found	..
	Matira, coaly lens 145 chain due west of Trig. Apotu	N55/401715	206	9092	10·0	? trace	10

TABLE 2—Boron and Ash Contents of South Island Mine Samples. The Coal Type of Samples from Greymouth is Indicated by J (James) B (Braehead) or S (Strongman). These letters, and Rank Nos (shown in brackets in "Coal Rank" column for Greymouth bituminous coals) are after Wellman (in Gage, 1952, pp. 78–104).

Mine	Coalfield	N.Z.M.S. 1	Type of Sample	Coal Rank	Analysis C.S. No.	Ash (%)	Determined B_2O_3 in Ash (%)	Calculated B_2O_3 in Coal (p.p.m.)
Blackburn	Buller	S24	Composite	Bituminous	1–16	2·2	0·41	90
Denniston	,,	,,	R.O.M.	,,	231	3·3	0·16	50
Millerton	,,	,,	,,	,,	232	3·3	0·08	30
Stockton	,,	,,	,,	,,	404	4·0	Nil	..
Burnwell	Reefton	S38	Top 36′ 8″ of seam	Sub-bituminous	221–225	1·4	2·73	380
,,	,,	,,	Bottom 5′ 7″	,,	226	5·1	0·64	330
Blackball	Greymouth	S44	R.O.M. (J)	Bituminous (14)	468	2·4	1·07	260
Braehead	,,	,,	Composite (B)	,, (15)	179–182	1·9	0·48	90
Dobson	,,	,,	R.O.M. (J)	,, (20)	211	5·6	trace	10
Fauth and party	,,	,,	Composite (S)	,, (13)	199–202	5·6	0·13	70
Goldlight	,,	,,	R.O.M. (S)	,, (19)	432	3·4	0·18	60
Gorge	,,	,,	(S)	,, (21)	431	11·4	0·06	70
Harrisons	,,	,,	Composite (S)	,, (14)	173–178	4·8	0·06	30
Liverpool	,,	,,	R.O.M. (S)	,, (20)	217	2·6	0·12	30
Old Runanga	,,	,,	(S)	,, (19)	429	7·2	0·09	60
Paparoa No. 2	,,	,,	(S)	,, (24)	126	2·3	Nil	..
,,	,,	,,	(S)	,, (24)	127	2·2	Nil	..
Strongman	,,	,,	R.O.M. (S)	,, (15)	216	2·2	0·85	190
Wallsend	,,	,,	(J)	,, (20)	218	9·1	trace	10
Shepherds Creek	Central Otago	S133	Shaly coal	Sub-bituminous	329	16·8	0·28	470
,,	,,	,,	Good coal	,,	330	7·1	0·44	310
Kaitangata	South Otago	S179	R.O.M.	,,	278	5·5	1·40	770
Wangaloa	,,	S180	18 ft seam	,,	275–277	3·4	1·08	370
"Mataura"	Southland	S178	Composite dist.	Lignite	261–266	4·7	0·54	250
Linton No. 1	Ohai	S168	R.O.M.	Sub-bituminous	242	3·7	0·60	220
Birchwood	,,	,,	,,	,,	249	5·3	0·10	50
Star	,,	,,	,,	,,	252	4·2	0·39	160
Black Lion	,,	,,	,,	,,	256	6·5	0·50	320
Black Diamond	,,	,,	,,	,,	257	4·3	0·75	320
"Ohai" ash	,,	,,	Composite dist.	,,	J2402	..	0·63	..

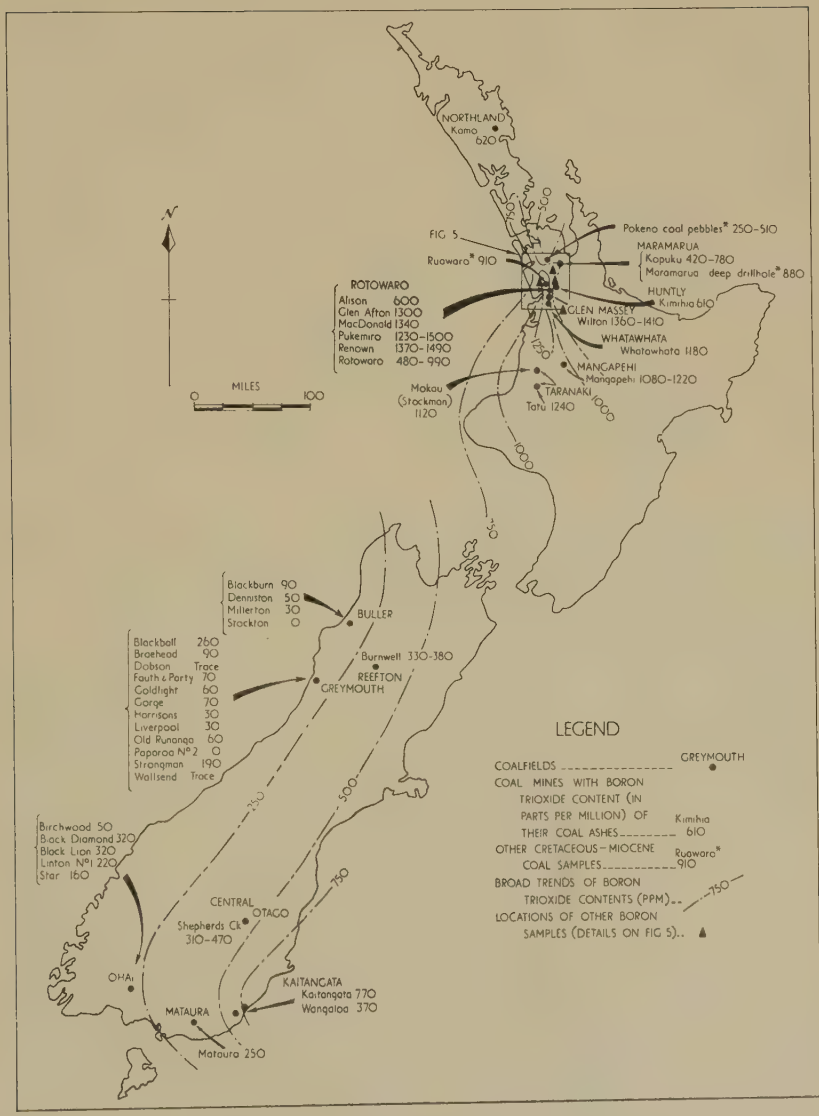

FIG. 1—Location of New Zealand coal ash samples for which the boron contents are known.

TABLE 3—Proximate and Ultimate Analyses of Samples from Rotowaro Nos. 1 and 3 Mines, Arranged in Order of Boron Content of Ash

Sample	Boron Trioxide Content		Proximate Analysis						Ultimate Analysis				
	Of Coal (p.p.m.)	Of Ash (%)	Ash (%)	Moisture (%)	Volatile Matter (%)	Fixed Carbon (%)	Calorific Value (B.t.u./lb)	Sulphur (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)	Oxygen (%)
CS302	890	3.42	2.6	16.5	39.6	41.3	9,860	0.3	72.7	5.0	1.2	0.4	20.7
CS311	870	3.36	2.6	16.4	44.0	37.0	9,810	0.3	72.0	5.0	1.0	0.3	21.7
CS312	840	3.11	2.7	14.1	41.8	41.4	10,480	0.3	73.3	5.4	1.0	0.4	19.9
CS310	900	2.57	3.5	17.1	42.9	36.5	9,580	0.3	72.2	4.9	1.0	0.3	21.6
CS301	480	2.53	1.9	16.3	40.3	41.5	9,780	0.3	71.8	4.9	1.2	0.3	21.8
CS313	990	2.25	4.4	15.4	39.4	40.8	9,880	0.3	72.3	5.1	1.1	0.4	21.1
CS300	830	2.08	4.0	16.1	38.9	41.0	9,590	0.3	71.7	4.8	1.1	0.4	22.0

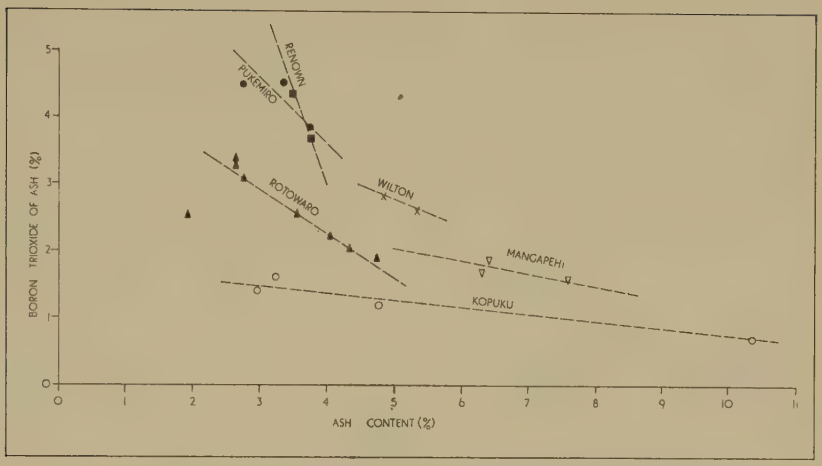

FIG. 2—Relation between boron and ash contents, North Island mines.

TABLE 4—Boron Contents, in p.p.m. of Coal, for Samples from Those New Zealand Mines from Which More than One Determination is Available

Mine	Boron Trioxide Content of Coal (p.p.m.)			
Paparoa No. 2*	0	0		
Shepherds Creek*	310	470		
Burnwell*	330†	380†		
Kopuku Opencast	420	530	580	780
Rotowaro No. 1	480	830	890	
Rotowaro No. 3	840	870	900	
Rotowaro Combined‡	*920*	*990*		
Mangapehi	1080	1220	1220	
Pukemiro	1230	1440	1500	
Wilton	1360	1410		
Renown	1370	1490		

NOTES—*South Island Mines.

†Of all samples in this table those from Burnwell probably show the greatest range in contents of ash (5·1% and 1·4%) and of boron (0·64% and 2·37%) when expressed as a percentage of coal ash. The difference in boron contents expressed as p.p.m. of coal is insignificant.

‡*"Rotowaro Combined"* figures in italics are for run-of-mine samples of mixtures of coal from Nos. 1 and 3 mines.

Of the other constituents of coal ash only the lime content appears to reflect that of boron to any marked extent. Table 5 shows a strong tendency, in both North Island and South Island, for coal ashes that are rich in boron to be rich also in lime.

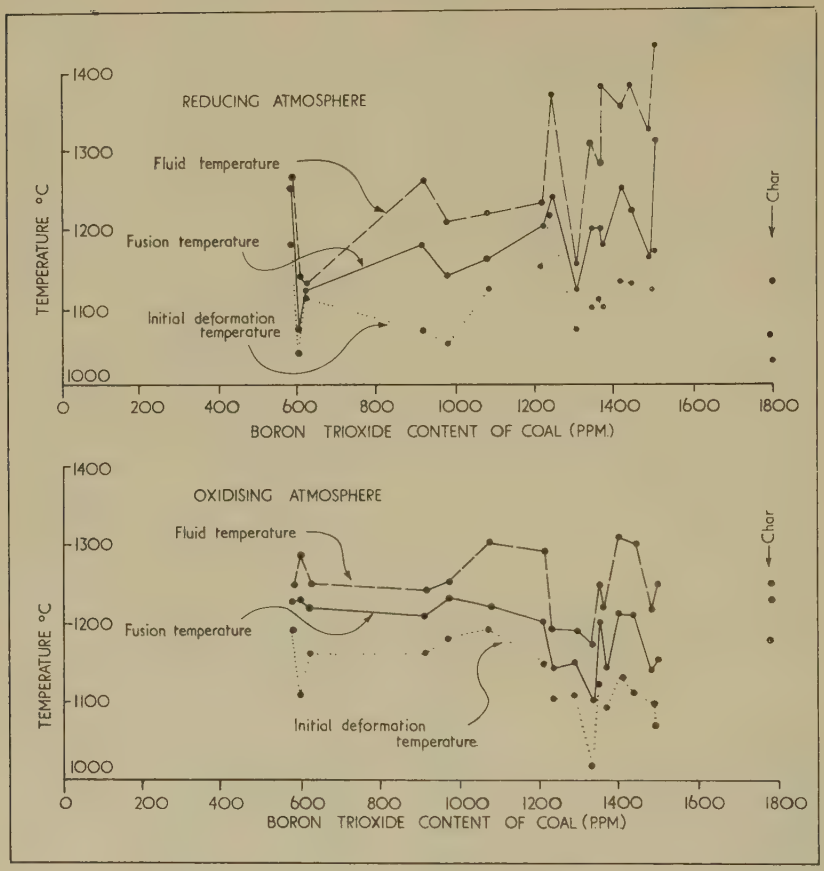

FIG. 3—Relation between ash fusion temperature and boron content, North Island mines.

Effect of Carbonisation

Table 1 includes eight samples from Rotowaro Mine which average 3·3% ash and 840 p.p.m of boron trioxide in the coal. A single sample of char from the Rotowaro Carbonisation Works (which uses Rotowaro coal predominantly) showed 7·6% ash and 1,790 p.p.m. of boron. The close similarity of the percentage increases of ash and boron, which were 130% and 113% respectively, implies that boron is not driven off appreciably during carbonisation.

Variation within a Seam and with Seam Depth

Three samples were collected from different parts of the seam at Rotowaro Nos. 1 and 3 mines and at Kopuku Opencast (Fig. 4). No consistent relation is evident between the boron content of a sample and its position

TABLE 5—Relation between Calcium and Boron Contents of Coal Ashes

Range of Boron Trioxide Content in Ash (%)			0–1	1–2	2–3	3–4	4–5
North Island Only	No. of Samples		1	2	4	1	3
	Lime Content (%)	Maximum	21.2	21.0	21.5	28.0	34.5
		Average	21.2	18.8	19.3	28.0	33.4
		Minimum	21.2	16.6	15.8	28.0	32.5
North and South Islands	No. of Samples		21	4	5	1	3
	Lime Content (%)	Maximum	25.3	23.8	21.5	28.0	34.5
		Average	6.9	16.2	19.1	28.0	33.4
		Minimum	0.2	3.4	15.8	28.0	32.5

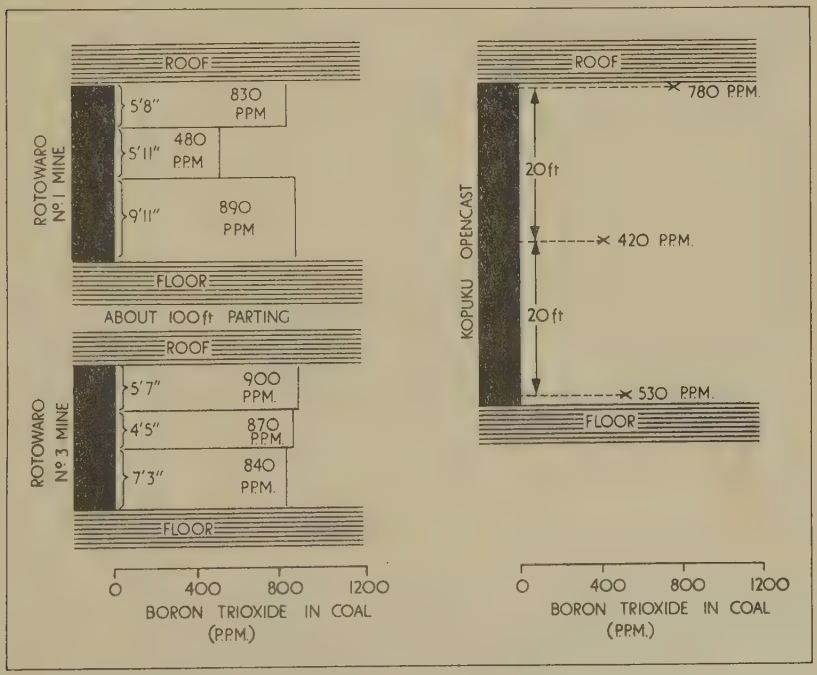

FIG. 4—Boron content of samples taken at different positions in seam. Those from Rotowaro Nos. 1 and 3 mines were channel samples; those from Kopuku Opencast were grab samples.

in the seam. Furthermore, the similarities of boron content for Rotowaro Nos 1 and 3 mines, which work different seams, are more striking than any differences that might be presumed to result from their being 100 ft apart vertically. Hence it can be inferred that small differences of stratigraphic position, either in the same seam or within different seams up to at least 100 ft apart, have no effect on boron content.

The deepest North Island coal sample that was analysed was collected from 1,570 ft below sea level in drillhole 1773 (Maramarua Coalfield). Its boron trioxide content (880 p.p.m.) is slightly higher than that of the nearest mined coal at Kopuku Opencast (420–780 p.p.m.), but the difference is certainly not as significant, having regard to distance apart, as exists for example between Alison and Rotowaro mines on the one hand and Renown and Pukemiro on the other (Fig 5).

Geographic Distribution

Figure 5 shows the distribution of boron in Eocene and Miocene coals in the central and northern Waikato coalfields, together with the relative position of other North Island samples. The highest values were found in samples along a north-trending zone, through Renown, MacDonald, Glen Afton, Pukemiro, and Wilton mines, which is parallel to the main structural trends in this region (MacPherson, 1946, map 2). To the east of this zone, and to the west to a lesser extent, there is a rapid decrease in boron content, far more pronounced than in a southerly direction where values at Whatawhata, Mangapehi, Tatu, and Mokau are almost as high as in the richest area of the Waikato coalfields. Thus the zone of maximum boron content appears to be narrow and richest in the north (Renown to Pukemiro), and thence to flare out widely southwards (with only slightly reduced values) to embrace all mining areas for which boron contents have been determined.

Fig. 1 shows the broad distribution of boron in Cretaceous to Miocene coals throughout New Zealand. The maximum values for the Waikato and Taranaki coals are striking. Only two samples of mined coal from the South Island (Kaitangata 770 p.p.m, and Shepherds Creek 470 p.p.m.) exceed the lowest corresponding value that is known from the North Island (420 p.p.m.). Within the South Island the highest known values are in the south-east, and there is a broad tendency throughout for the boron content to decrease westwards.

North Island Stratigraphic Distribution

Neither of two samples of Mesozoic coal showed more than a possible trace of boron. Both were collected to the west of the boron-rich zone of the younger coals (Fig. 5); but the fact that no North Island coal of Eocene to Miocene age contained less than 250 p.p.m. of boron trioxide, suggests that the lack of boron in Mesozoic coal is due to factors other than location.

The Eocene and Miocene coal measures which together account for all

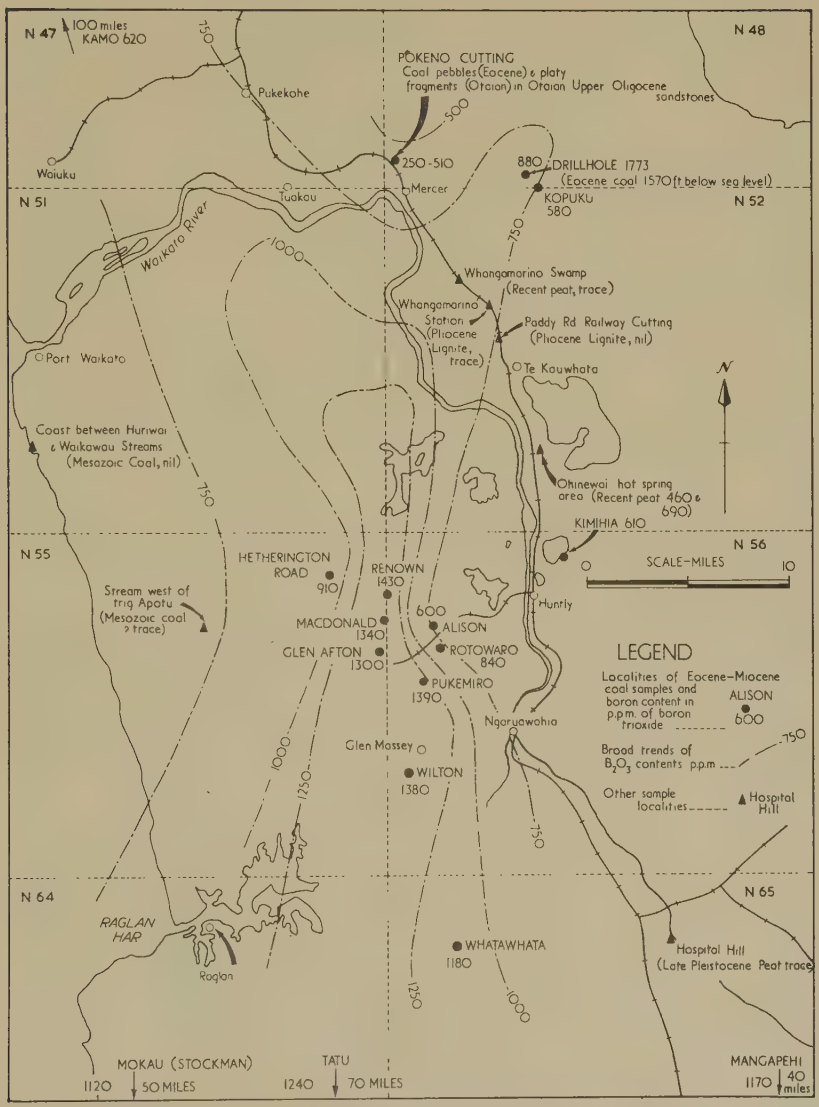

FIG. 5—Distribution of boron content in coal from northern and central Waikato Coalfields. The boron trioxide contents in parts per million of the coal, are taken from the average values in Table 4 where more than one sample is available.

coal production, are markedly different from each other. The former (Te Kuiti Group of the Waikato Coal Region) contain lenticular seams of coal of variable, although often considerable thickness. They were laid down under wholly terrestrial conditions in the low-lying areas of a land that included hills of Mesozoic greywacke of several hundreds and possibly thousands of feet in height. Marine beds overlie the coal measures at stratigraphic intervals ranging from a few feet to a few hundred feet in different areas. The Miocene coal measures (Mokau Group of the Taranaki Coal Region) contain relatively thin coal seams of very constant thickness. They were laid down during temporary, terrestrial conditions in a dominantly marine sequence, several thousands of feet thick, and no Mesozoic greywacke hills would have been present nearby. In spite of these considerable facies differences, the boron contents of the Miocene coals of Mokau and Tatu are very similar to those of the nearest Eocene coals at Whatawhata and Mangapehi (Fig. 5).

Coal pebbles at Pokeno contain plant microfossils similar to those of the coals of the Maramarua Coalfield, and their analyses are also similar. They are therefore presumed to have been derived from an upper Arnold (Eocene) coal seam, although they now occur in basal Otaian (Oligocene) sandstones (Kear, in press). Their boron trioxide content (510 p.p.m.) is broadly similar to that of Kopuku coal (Maramarua Coalfield). Small plate-like coal fragments, which accompany the pebbles and may represent bark or wood deposited in the Otaian, contain 250 p.p.m of boron trioxide.

Seven lignites and peats of Pliocene, Pleistocene, and Holocene age were collected from different parts of the Waikato Valley. Five were collected away from any known hot-spring activity and all contained no more than a trace of boron. The other two were deliberately collected close to an area of hot-spring activity at Ohinewai and contained 460 p.p.m. and 690 p.p.m. of boron trioxide. These values are of the same order as would have been expected in Eocene coal in that area (Fig. 5).

South Island Comparisons

Of the South Island coals (Table 2, Fig. 1), only three mines were represented by as many as two samples, and each pair of analyses show boron content (as p.p.m. of coal) of similar order.

South Island coals show greater rank variation (from lignite to bituminous coal in this survey) than those from the North Island. Fig. 6 illustrates the relation between rank and boron content and shows that bituminous coals contain less boron than sub-bituminous coals, and that the higher rank bituminous coals contain least of all. This effect of rank is so marked that any possible differences that might be due to type are obscured at least with the present number of samples. What little can be gleaned from the Greymouth coal rank and type variations (Table 2), leads to the initial inference that type bears little or no relation to boron content.

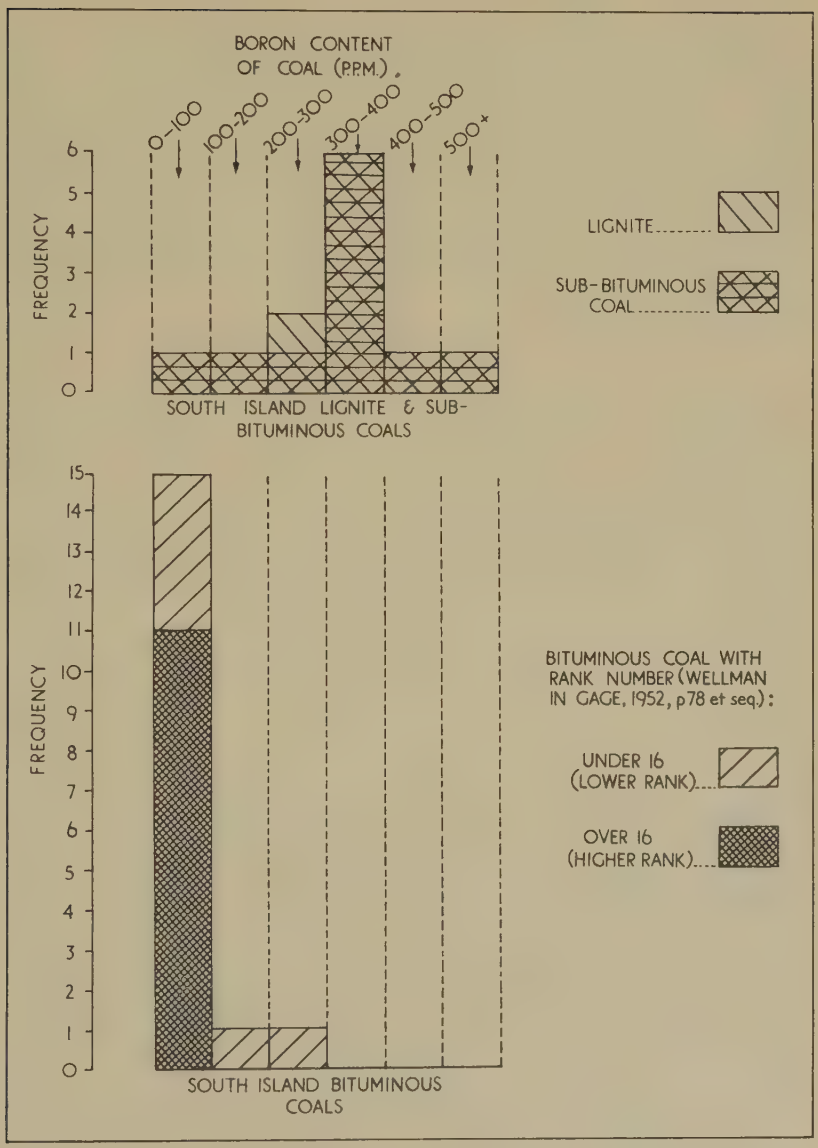

FIG. 6—Frequency of boron contents (at 0·2% B_2O_3 intervals) for South Island coals, grouped on a rank basis.

SOURCES AND EMPLACEMENT OF BORON

The excessive richness in boron of coal ashes from the North Island of New Zealand, when contrasted with those from overseas, may be partly apparent, due to the combined effects of the coal's sub-bituminous rank and relatively low ash content. However, even allowing for this fact, New Zealand's coals are among the richest in boron in the world and this must presumably be due to the unusual local effectiveness of one or more sources of boron. Insufficient data are yet available to identify the most important of these sources with certainty, but there are sufficient data to allow useful comment on the probable effectiveness of several hypothetical sources, and on times and methods of emplacement. The significant results that require explanation are summarised initially below.

Summary of Significant Results

1. Of all the items of normal coal and coal ash analyses, only the ash content of coal and the calcium content of ash appear to reflect the boron content of the coal.

2. Boron content of a coal is broadly constant locally, in the sense that far greater difference can exist between coals from different mines than do exist between coal samples from a single mine.

3. In the Renown-Pukemiro area of the Waikato, the distribution of coals with maximum boron content is linear, relatively narrow, and parallel to the major structural trends.

4. South Island mined coals and North Island Mesozoic coal show that the boron content of bituminous coals is lower than that of sub-bituminous, and is a minimum in coals of the highest rank. The latter reflect no apparent effect of type in their boron content.

5. In the North Island, no significant differences in boron content exist between Eocene and Miocene coals in spite of very different depositional environments, one, inland swamps with surrounding "greywacke" hills or mountains, the other, dominantly marine, apparently from high land.

6. Small differences of stratigraphic position, either within the one seam, or between different seams up to 100 ft apart, have no apparent effect on boron content.

7. Pliocene to Holocene peats and lignites of the Waikato Valley generally contain no more than a trace of boron.

8. Holocene peat samples, deliberately collected from near a hot spring, contain boron in quantities similar to that found in mined coals.

Sources Contemporaneous with Deposition

BORON-RICH PLANTS

A primary origin, from boron-rich plants, is unlikely, both because the modern flora, which broadly resembles that of the lower Tertiary coal measures described by Couper (1953), has formed Pliocene-Quaternary peats and lignites that normally lack boron, and because there is no apparent effect of type variations on boron content in bituminous coals.

COLD WATERS CONTAINING BORON DERIVED BY LEACHING

The presence of boron in New Zealand greywackes and argillites has been recorded by Reed (1958, pp. 39–40), and tourmaline is well known in South Island granites, gneisses, and schists (e.g., see Morgan, 1927, pp. 101–2). Boron, leached by surface and ground waters from higher country consisting of such rocks, might have been redeposited in lowland peat swamps. Certainly, boron has been identified in surface water draining from greywacke rocks at the present day (Schofield, 1960, p. 99), and a similar source may have been responsible for part of the boron in New Zealand coals. This source cannot explain the very high boron contents of Miocene coal measures of the Taranaki Coal Region, however, because their depositional environments included no nearby "greywacke" terrain. Hence, although cold waters with leached boron may account for some boron in coal, it seems unlikely to be the major cause of New Zealand's very high value.

HOT SPRINGS

It appears likely that hot springs can deposit boron in present-day peat (see below). A source from hot springs at the time of peat accumulation seems an inadequate explanation for boron-rich coal, however, both because of the absence of any supporting evidence of contemporaneous volcanism or hot spring activity in North Island coal measures, and because the similar order of richness in both Eocene and Miocene coals would require the coincidence of similar orders of hot spring activity during both these periods.

SOURCES SUBSEQUENT TO DEPOSITION

SEA OR CONNATE WATER

Sulphur is commonly presumed to be introduced into coal seams from sea water which percolated downwards through the coal measures following a marine transgression. A broad inverse relation has been shown to exist between the sulphur content of a coal seam and its stratigraphic depth below marine beds (see Wellman *in* Gage, 1952). Boron, undoubtedly present in sea water (Clarke, 1924, p. 123), may have been introduced similarly into New Zealand coals from downward percolating sea water. In favour of this source as of major importance are the facts: (1) that sulphur appears to be fixed readily at the beginning of coalification, (2) that boron-rich coals are also rich in calcium, which is itself the third most common metallic element in sea water (Clarke, 1924, p. 127), and (3) that marine beds overlie most of New Zealand's boron-rich coal seams at no great stratigraphic interval. Opposing evidence includes the facts (1) that there is no observable decrease of boron as the stratigraphic interval increases, and (2) although the marked increase in boron content from Rotowaro to Renown and Pukemiro corresponds to a decrease in stratigraphic thickness between coal seam and marine beds, the thickness is even less at Hetheringon Road and at Kamo where the boron contents are similar to those at Rotowaro.

HOT-SPRING ACTIVITY

There can be little doubt that the boron in the Ohinewai peat was emplaced as a result of nearby hot-spring activity. Quite apart from the facts that boron was present in only those peat and lignite samples that were collected near hot springs, and that boron is a well known constituent of hot-spring waters (Healy, 1942; Fleming, 1945, p. 269), Schofield (1960) has shown that, in the Waikato area, warm magmatic ground waters contain considerably more boron (21·5 to 112·0 p.p.m. as HBO_2) than do cold ground or surface waters (0 to 1·0 p.p.m.) in the same area. Whether the boron was derived from a volcanic source or was leached by ascending hot water cannot be determined at present.

If boron in a modern peat can be attributed to hot-spring activity, then the possibility that the boron in New Zealand coals came from a similar source, as Rafter (1945) has suggested, must be seriously considered. Additional facts in favour of such a theory are, that the narrow linear distribution of maximum boron contents in the Renown-Pukemiro area, which is parallel to major structural trends, could be explained in terms of hot-spring activity along a fault; that volcanic activity and boron richness are both greater in the North Island than in the South Island; and that the maximum andesitic and basaltic volcanic activity, with which are associated the springs richest in boron (Schofield, 1960), occurred in the North Island coalfields area in late Miocene to lower Pliocene times (Kear, 1959), i.e., between the formation of the evenly boron-enriched Eocene and Miocene coals and the generally barren upper Pliocene lignites. Against such a theory are the facts that a very even enrichment of the groundwater would be necessary to ensure the observed even richness of coals from relatively widely spaced mines; that no independent evidence of hot-spring activity is known from the Renown-Pukemiro area; and that the emplacement would take place in coal rather than in peat, which might be considered as less reactive. The small amounts of boron in South Island coals might have other sources, including possibly leaching and deposition from "tectonic" hot spring waters.

ASH SHOWERS

A possible source from rainwater percolating downwards through ash showers is considered to be unlikely; both because the expected downward decrease in boron content has not been observed either in individual coal seams or between seams at different depths; and because the known ash showers above the coal measures also overlie the Pliocene lignites at Whangamarino which contain no more than a trace of boron.

MECHANISM OF EMPLACEMENT

Whatever its initial source, the boron was probably emplaced from solution. The enriched waters may have been restricted to a small area near a single hot spring (e.g., Ohinewai), or may have been widespread, resulting for example from the enrichment of ground water by numerous hot springs

or by a considerable admixture of percolating sea water. Widespread ground-water enrichment could presumably have led to the broadly uniform boron contents of Eocene and Miocene coal seams.

Although boron was first detected in coal ash, it seems more likely to have been precipitated in the seam by virtue of the carbonaceous content of the coal rather than its mineral content. Not only is this implicit in the recognition of broadly constant boron contents of coal from one area, regardless of ash content, but the carbonaceous mudstone above the seam at Kopuku failed to show any trace of boron such as is present in the coal (Table 1).

The lower boron contents of coal of higher rank could be due either to an expulsion of boron as coalification progressed, if emplacement had already occurred, or to an increasing impedance to ground-water circulation as permeability became reduced, if emplacement took place after coalification. In the latter case, there would be a relation between the boron content of a coal and its natural ability to hold water, both of which fall off as rank increases from sub-bituminous through the bituminous range.

CONCLUSIONS

Hot spring waters can apparently enrich nearby peats in boron to a degree similar to that of New Zealand's unusually boron-rich coals. Although several sources may contribute boron to coal, the source (or sources) that make New Zealand coals among the richest in the world, is probably either hot spring activity or/and sea water percolation. The former hypothesis appears the more likely on present evidence, although it involves enrichment of coal in Miocene-Pliocene times from ground water that was itself enriched from extremely numerous but quite hypothetical volcanic hot springs. If the source were sea water, enrichment would have taken place at the peat stage soon after the marine transgression over the coal measures, in the same way that coal seams become enriched in sulphur. The unusual richness of New Zealand coals, when comaperd for example with British and North American coals of Carboniferous age, might then be traceable in some way to their younger age (Senonian to Miocene, Suggate, 1956) and different sea water conditions. The geographical and stratigraphic distribution, however, give no supporting evidence for such an initial source.

Any future research might profitably aim initially at experimental attempts to enrich coals, as opposed to peats, from boron-rich water.

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THE INFLUENCE OF SALINITY ON THE RATE OF OXYGEN CONSUMPTION OF YOUNG QUINNAT SALMON (*Oncorhynchus Tschawytscha*)

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Summary

1. The reported difference in growth rate between quinnat salmon (*Oncorhynchus tschawytscha*) in fresh water and in sea water under natural conditions, is supported.

2. The rates of oxygen consumption of one-year-old quinnat salmon in fresh water, in half sea water, and in sea water were measured under similar conditions and were found not to differ significantly.

3. Evidence suggests that a large change in respiration rate accompanying a change in the osmotic strength of the surrounding medium of an aquatic animal may result from an initial breakdown in osmoregulation.

Introduction

Quinnat salmon were introduced into New Zealand between 1901 and 1906. At present, spawning runs take place in most of the snow-fed rivers on the east coast of the South Island. Besides these anadromous populations, landlocked quinnat salmon are found in certain South Island lakes, which may or may not be accessible to salmon from the sea.

Landlocked quinnat from Lake Coleridge average 2 to 4 pounds in weight at maturity, while sea-run fish in nearby rivers average 10 to 12 pounds (Table 1, Prof. E. Percival, pers. comm.). Landlocked sockeye salmon (*O. nerka*), Atlantic salmon (*Salmo salar*) and alewives *Pomolobus pseudoharengus*) are smaller than the anadromous forms of these species (Hoar, 1952) as are also brook trout (*Salvelinus fontinalis*) (Wilder, 1952). The reason for these size differences between the anadromous and landlocked forms of these fish is not clear.

Table 1—Size at Maturity of a Sample of Sea-run Quinnat (Waimakariri River) and a Sample of Landlocked Quinnat (Lake Coleridge)

Year	Place	Mean Length	Range	Mean Weight	Range	No. of Fish
1944	Waimakariri R	757 mm	635–940 mm	4·89 kg	3·62–7·25 kg	33
1954	Hennah Stream (L. Coleridge)	475 mm	381–533 mm	0·96 kg	0·50–1·72 kg	86

There is some experimental evidence that salinity *per se* influences the growth of fish. Canagaratnam (1959) found that certain salmonids, coho, chum, and sockeye salmon, when kept under standard conditions of food supply and temperature, grew more rapidly in dilute sea water than in fresh water. In one series, 50 coho salmon (*O. kisutch*) grew in average weight from 1·007 grams to 1·8 grams in 7 weeks in fresh water and a similar number of fish in sea water of 18‰ salinity, grew in average weight from 1·007 grams to 2·4 grams in the same period.

Gibson and Hirst (1955) found that fresh water guppies (*Lebistes reticulatis*) grew slightly faster in quarter sea water than in fresh water.

In the course of the present experiment the growth rates of young quinnat held in fresh water, in half sea water (a solution containing equal parts of sea water and fresh water), and in sea water, under similar conditions and fed similar amounts, were determined. The mean specific growth rates of each group of 8 fish are shown in Table 2. Although the fish in half sea water grew faster than those in fresh water, the difference was found to be not significant by the t-test. The fish in sea water were the slowest growing; two did not grow at all.

TABLE 2—Mean Specific Growth Rates* in Weight (8 August – 28 September) of Groups of Eight Young Quinnat in Fresh Water, in Half Sea Water, and in Sea Water

Group	Mean Specific Growth Rate	Standard Deviation
FW	5.11	1.84
½SW	6.98	1.22
SW	2.55	3.03

*(Specific growth rate $= \frac{\log_{10} W_2 - \log_{10} W_1}{T_2 - T_1} \times \frac{2{\cdot}3026}{1} \times \frac{100}{1}$, W in grammes. T in days.)

Hoar (1953) referring to landlocked sockeye salmon (*O. nerka*) says: "Although sockeye have a resistance to fresh water which chums lack, and frequently mature in lakes where they spend their early life, there is evidence of osmotic stress in their relatively reduced growth rate (Hoar, 1952) and marked thyroid stimulation is apparent during the spring of smolt transformation. (Hoar and Bell, 1950)."

There have been numerous experiments to examine the relation between the osmotic pressure of the external medium and the respiration rate of aquatic animals. For a review of the literature see Wikgren (1953), Beadle (1957), and Gross (1957). Some investigators (e.g., Beadle, 1931; Hiscock 1953b) have found that the respiration rate varies directly with the difference in osmotic pressure between the body fluids and the surrounding medium. According to Wikgren (1953), Graetz (1931) found that the

stickleback (*Gasterosteus aculeatus*) respired at a higher rate in fresh water than in sea water, whereas Maloeuf (1938) found that *Fundulus heteroclitus,* a fish like the stickleback in its ability to live in either fresh water or sea water, did not respire at different rates in the two media.

As part of a study of the growth rates of young quinnat salmon kept in waters of different salinities, respiration rates of resting fish were measured to determine whether they were affected by salinity.

METHODS AND MATERIALS

The fish used were netted on 3 August 1957 from a pond at the Islington Freezing Works, Christchurch, at the end of a stock-water race from the Waimakariri River. The initial size of the fish, and the scales taken from them when they were killed, indicated that they were one year old when netted. Although parr marks were still visible on some of the fish, extensive sivering indicated that the parr-smolt transformation was in progress or completed. The fish were held in fresh water until 8 August when four were placed in each of six aquaria, two of which contained fresh water, and the other four, equal parts of fresh and sea water.

The fresh water used throughout the experiments was obtained from the Christchurch City artesian supply (sample analysis, Table 3) and was stood and aerated at room temperature and pressure for 2 hours before placing fish in it. The sea water was obtained from Taylor's Mistake, Banks Peninsula. On 23 October 1957, the chlorinity was 19·6 grams per kilogram (salinity = 35·4 grams per kilogram).

TABLE 3—Analysis of Sample of Water from Christchurch City Water Supply, March 1957

	P.p.m.
Chlorine in chlorides	10
Nitrate nitrogen	1·2
Nitrite nitrogen	Nil
Ammoniacal nitrogen	Nil
Albuminoid nitrogen	Trace
Oxygen absorbed in 4 hours at 80°F	Trace
Total solids	116
Iron (Fe)	Nil
Hardness – Total	65
pH	7·6
Smell	Faint
Appearance	Clear and bright
Deposit	A small deposit of organic matter and siliceous particles.

The six rectangular glass aquaria used were identical in construction and each had a capacity of 56·0 litres. The aquaria were arranged near each other. They were evenly lit, but no attempt was made to control the duration of daily illumination. Each aquarium was aerated continuously by a stream of air bubbles from a coarse capillary tube.

On 16 August the half sea water in two aquaria was replaced by sea water. Thus the eight fish finally placed in sea water had been given eight days to adapt to half sea water. The fish were fed live *Paracalliope fluviatilis,* a small fresh-water amphipod, at the rate of 0·1 to 0·2 grams per gram of fish per day. The fish were fed daily except on about every eleventh day, when the water was changed and the fish photographed to record growth. The fish were photographed in a perspex chamber placed inside the aquaria. All faeces and dead amphipods were siphoned once a day from the aquaria. Water temperature was recorded on a maximum-minimum thermometer kept immersed in an aquarium in the same room. Between 18 August and 25 October a maximum temperature of 19·0°C and a minimum of 12·0°C were observed. Three of the fish died after 28 September and before their respiration rates had been determined.

The apparatus used to measure the rate of oxygen consumption was similar to that described by Keys (1930) and used extensively by Wells (1935). Water was passed at a known rate over the fish in a closed container and the oxygen content of the water before and after it had passed through the container was determined. The rate at which the fish removed oxygen from the water could then be calculated. Two significant alterations in the apparatus were in the type of respiration chamber used, and in the method of collecting the water sample. It was observed that when a glass tube was used as a respiration chamber, the curvature of the glass prevented the fish from attaining a natural resting position. Flat-bottomed perspex respiration chambers were therefore built. These chambers were a little longer than the longest fish, and triangular in cross-section in order to reduce their volume (Fig. 1). To shield the fish from outside disturbances, the respiration chambers were enclosed in a light-proof wooden box, which rested on a sponge rubber mat 6 cm thick.

When a water sample was to be collected the water was diverted into a bottle filled with kerosene, displacing the kerosene into a second bottle filled with water (Fig. 1). By lowering the outlet tube when the water was flowing into the collecting bottles, it was possible to maintain a constant rate of flow whether or not a sample was being collected. The main advantage of this over previous methods is that no water is lost in collecting a sample.

A modification of the Winkler technique described by Ellis, Westfall and Ellis (1946) was used to determine the oxygen content of the water samples. One gram of sodamide was added to every 100 cc of KOH-KI reagent when half sea water and sea water were being analysed, to remove nitrite (Truesdale, Downing and Lowden, 1955). The end-point of the thiosulphate-iodine titration was found by the amperometric method of Knowles and Lowden (1953).

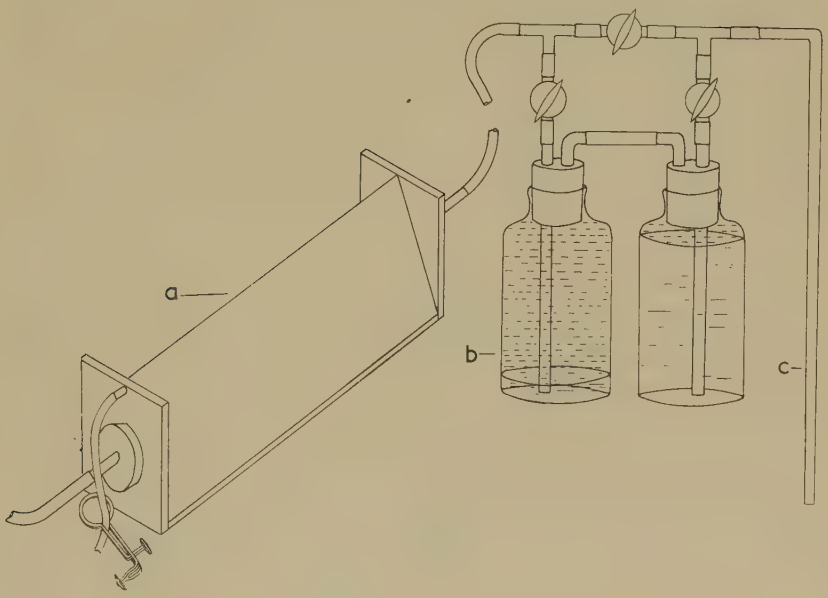

FIG. 1—Part of apparatus used to measure the rate of oxygen consumption of young quinnat salmon (a, respiration chamber; b, sample bottle with layer of kerosene; c, outlet tube).

Procedure

The tap water for the experiments was stood at room temperature and pressure and stirred for at least eight hours before use.

The oxygen consumptions of two fish were usually determined at the same time. The fish were each placed in a respiration chamber at about 11.30 a.m., the chambers placed in the wooden box, and the rate of flow of water adjusted to provide a good supply of oxygen while the fish were respiring actively after being handled. The fish almost invariably ejected bubbles of gas from their mouths within 1–2 hours after being placed in the respiration chambers. At 2.30 p.m. all the bubbles were removed from the respiration chambers via the tube provided for this purpose; the lid was placed on the box and the rate of flow of water was adjusted so that the fish removed about a third to a half of the oxygen in the water. Sampling and analysis were commenced at about 7.30 p.m. and continued until about six sets of samples had been analysed, about 5 hours later. Samples were collected simultaneously of the water which had passed through the chambers and of the water which had by-passed them. The time taken for the sample bottles to fill was measured with a stop-clock.

The fish were not fed during the 24 hours prior to the determination of their rate of oxygen consumption. A temperature of 16·3°C ± 0·3°C was

maintained in the apparatus by passing the water through a coiled tube immersed in a thermostatically controlled bath.

Immediately after their respiration rates had been determined the fish were weighed to the nearest 0·25 gram.

The experiments were carried out between 2 October and 15 October 1957 and the aquaria were dealt with in the following sequence f.w., s.w., ½ s.w., s.w., ½ s.w., f.w.

RESULTS

Rates of oxygen consumption, expressed as milligrams of oxygen consumed per hour per fish, together with the weight of each fish, are given in Table 4.

TABLE 4—Rates of Oxygen Consumption in Milligrams of Oxygen Consumed per Hour per Fish, and Weights of Fish

Fish	Weight (g)	Oxygen Consumption in mç Oxygen/Hr/Fish						Mean
		1	2	3	4	5	6	
F.W. 1	21.3	2.84	2.75	2.97	2.91	2.68	2.98	2.855
2	33.45	4.24	4.77	–	5.08	4.56	4.62	4.654
3	31.05	6.95	5.59	7.08	6.60	5.56	–	6.356
4	21.25	2.78	2.12	2.51	2.82	2.92	–	2.630
5	25.0	4.69	4.28	4.14	4.13	3.93	4.19	4.227
6	20.9	3.56	3.63	4.51	3.94	4.25	3.85	3.957
7	28.8	4.39	4.25	–	4.32	5.84	5.26	4.812
8	25.3	3.55	3.84	7.94	4.91	8.98	8.15	6.228
½ S.W. 1	23.6	5.95	7.46	6.08	5.46	6.33	7.47	6.458
2	19.35	3.17	3.73	2.67	3.24	5.05	4.29	3.692
3	44.3	5.45	4.82	5.77	5.93	5.46	5.54	5.495
4	24.7	–	4.17	4.72	3.96	3.92	3.83	4.120
5	38.5	5.96	6.03	6.48	7.08	6.55	6.19	6.382
6	34.2	4.41	4.67	4.63	5.58	5.25	5.45	4.998
S.W. 1	14.6	3.38	3.19	2.48	2.72	2.74	3.22	2.955
2	18.1	3.25	3.56	2.79	2.40	3.15	–	3.030
3	24.85	3.75	4.01	4.05	3.93	4.08	3.80	3.937
4	17.4	3.18	3.03	4.48	2.83	3.55	3.54	3.435
5	21.0	4.02	3.35	3.17	3.10	2.97	3.10	3.285
6	14.85	2.68	2.34	3.16	3.39	3.36	2.78	2.952
7	35.4	4.73	4.54	4.92	5.08	4.42	4.62	4.718

For fish, as for many other animals, the rate of oxygen consumption does not vary directly with the weight, but with a function of the weight W^r, r as a general rule lying between 2/3 and 1 (Fry, 1957). If M is the rate of oxygen consumption, the relationship may be expressed

$$M = bW^r$$

where b and r are constants for the group of animals concerned.

In Fig. 2, mean oxygen consumption in milligrams per hour has been plotted against weight in grams for each fish, both coordinates being logarithmic.

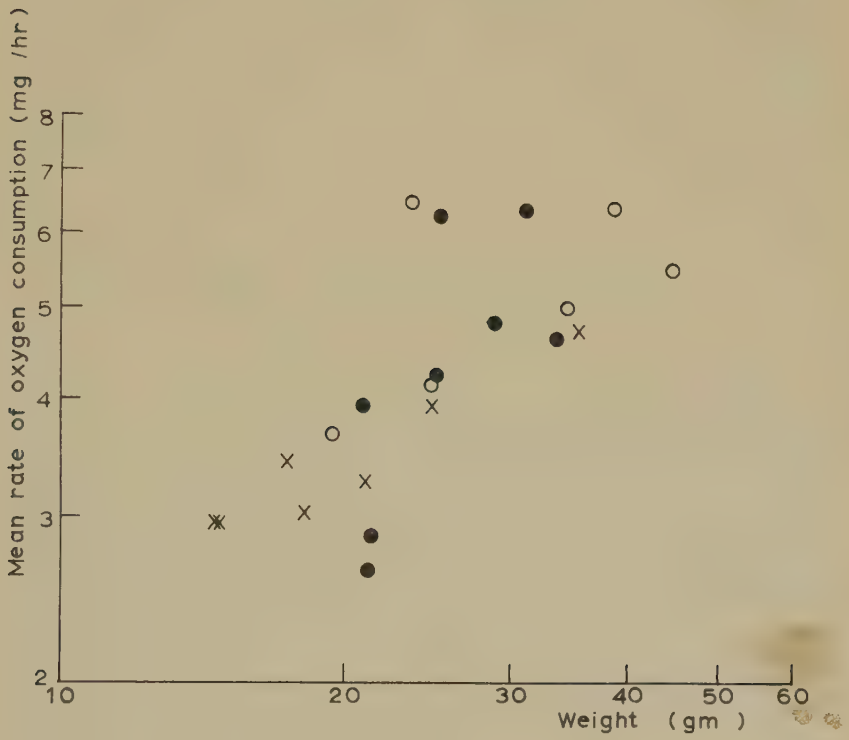

FIG. 2—Mean rate of oxygen consumption of young quinnat salmon plotted against weight. Fish in fresh water ●, in half sea water ○, in sea water ×.

The analysis of covariance technique was used to determine the significance of the difference between the rate of oxygen consumption of the three groups, this procedure allowing for the relationship between the rate of oxygen consumption and weight. The results of the analysis of covariance and the regression equation of logarithm of rate of oxygen consumption on logarithm of weight for each group, are set out in Table 5.

It was found that there was no significant difference at the 5% level of significance, between the mean log. rates of oxygen consumption of the groups after correcting for the regression of rate of oxygen consumption on weight.

TABLE 5—Results of Analysis of Covariance of Log. Rate of Oxygen Consumption on Log. Weight and Regression Equations

	Variance Ratio (F)	Degrees of Freedom (D.F.)	Significance (P)
Regression	12.31	1, 17	$0.001<P<0.01$
Difference between group means	0.7438	17, 2	$P>0.20$
Significance of difference of slopes	1.60	2, 17	$P>0.20$

Regression lines:

F.W. $Y = 1.259X - 1.14$

½ S.W. $Y = 0.405X + 0.1108$

S.W. $Y = 0.525X - 0.1478$

Y = Log.$_{10}$ rate of oxygen consumption.
X = Log.$_{10}$ weight.

DISCUSSION

Beadle and Cragg (1940), working with certain *Gammarus* species, came to the conclusion that in aquatic animals there must be active regulation of (a), the concentration of the body fluids, and (b) the concentration of certain ions within the cells. Ramsay (1954) pointed out that in freshwater animals possessing a body fluid, there were two principal sites of osmotic and ionic regulation. Firstly, organs specialised for the elimination of water and transport of ions will regulate the composition of the body fluids. Secondly, cell membranes will regulate the passage of water and ions between the body fluids and the interior of the cells.

It follows then that a change in the osmotic pressure of the surrounding medium could alter the metabolic rate of an aquatic animal in the following ways.

(a) A change in energy output by the osmoregulatory organs would be necessitated on thermodynamic grounds.

(b) Failure of the osmoregulatory organs resulting in a change in the concentration and/or composition of the body fluids might cause:

(1) A change in energy expended on osmotic and ionic regulation by all tissues and

(2) Changes in metabolic rate resulting from disturbances in the metabolic processes.

Equations for the minimum thermodynamic work expended on osmoregulation by an aquatic animal in a hypotonic medium have been presented by Potts (1954). He assumes that the animal possessed a semi-permeable covering and that the extra-renal salt loss was negligible. Potts calculated that minimum thermodynamic work performed by the fresh water *Eriocheir sinensis, Potomobius fluviatilus,* and *Anodonta cygnea* and found it to be 0·5%, 0·3%, and 1·2% respectively of the standard metabolic liberation of energy of each animal when in fresh water.

Large changes in the respiration rates of aquatic animals transferred to media of different osmotic strengths have been recorded and in some cases ascribed to a change in energy expenditure on osmoregulation (Beadle, 1931). Such changes in respiration rate have, however, often been accompanied by changes in body weight and in composition of the body fluids. Eels temporarily increased in weight when transferred to fresh water from sea water (Keys, 1933). When chum (*O. keta*) and coho (*O. kisutch*) salmon fry were transferred from fresh water to sea water, there was an initial increase in the chloride concentration of the blood (Black, 1951). Transfer of the freshwater mussel, *Hyridella australis*, from fresh water to dilute sea water, resulted in a rise in blood chlorinity, a fall in weight, and a decrease in respiration rate (Hiscock, 1953 a and b). In such cases it would appear that the osmoregulatory organs have failed to keep the body fluids constant in composition; an increase in energy expenditure would be necessary to return the body fluids to their previous composition.

Experiments by Wells and Ledingham (1940) on isolated muscle strips from *Arenicola marina* and *Nereis diversicolor* and by Pilgrim (1953) on isolated heart muscle strips from *Anodonta cygnea, Ostrea edulis,* and *Mytilus canaliculus,* demonstrated that a sharp drop in the salinity of the surrounding medium resulted in a temporary increase in tone in the muscle strips. It is possible that such an increase in muscle tone and consequent elevation of the metabolic rate might occur in intact animals when the body fluids are diluted by osmotic flooding.

With the technique employed in the present experiment no significant difference could be found between the rate of oxygen consumption of young quinnat in fresh water, dilute sea water, or sea water. This is what would be expected if the energy expended on osmoregulation was a small proportion of the total energy consumption as was calculated by Potts for the three freshwater invertebrates.

Where a change in the respiration rate of an aquatic animal has been correlated with a change in salinity, evidence suggests that it results from an initial breakdown in osmoregulation followed by a disturbance of tissue metabolism. In the present instance such an initial disturbance either did not occur or had disappeared before the respiration rates were determined.

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